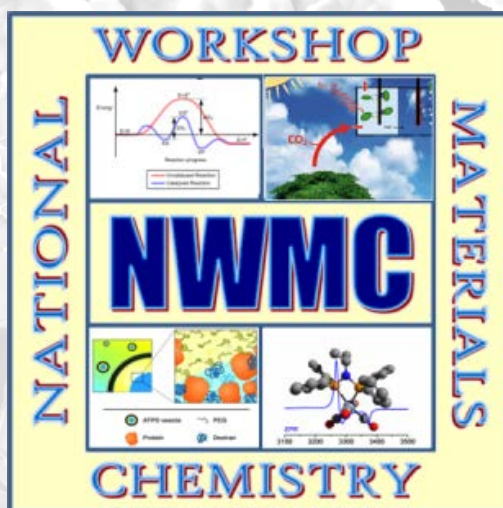**Proceedings of DAE – BRNS**

6th National Workshop on Materials Chemistry

Synthesis Strategies of Materials

NWMC-2023 (SYN-MAT)

October 13-14, 2023

Venue
DAE Convention Centre,
Anushaktinagar, Mumbai-400094, India

Organised by
Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai-400085, India
&
Society for Materials Chemistry, Mumbai

Supported by
Board of Research in Nuclear Sciences
Department of Atomic Energy
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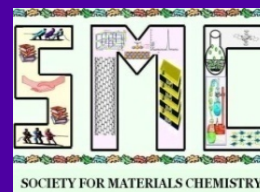Trombay, Mumbai-400085, India
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प्रस्तावना

हम प्रतिष्ठित "पऊवि–बीआरएनएस पदार्थ रसायनिकी पर छठी राष्ट्रीय कार्यशाला (एनडब्ल्यूएमसी - 2023)" में सभी प्रतिभागियों का स्वागत करते हैं। यह कार्य शाला पदार्थ रसायनिकी संस्था, मुंबई के सहयोग से रसायनिकी प्रभाग, भाभा परमाणु अनुसंधान केंद्र द्वारा आयोजित द्विवार्षिक कार्यशाला श्रृंखला का वर्ष 2023 का संस्करण है। इस वर्ष की कार्यशाला का विषय वस्तु "पदार्थ संश्लेषण की विधियाँ" है जिसे संक्षेप में "सिन-मैट" कहा जा रहा है। एनडब्ल्यूएमसी कार्यशाला श्रृंखला को वर्ष 2011 में "पऊवि – बीआरएनएस पदार्थ रसायनिकी पर पहली राष्ट्रीय कार्यशाला (एनडब्ल्यूएमसी)" के रूप में शुरू किया गया था और उसके बाद यह द्विवार्षिक श्रृंखला नियमित रूप से जारी है। अपनी स्थापना के बाद से, एनडब्ल्यूएमसी श्रृंखला को देशभर के युवा शोधकर्ताओं से बेहतरीन प्रतिसाद मिला है। यह कार्यशाला अग्रणी क्षेत्रों पर चर्चा के साथ-साथ उपयोगी और मौलिक पदार्थ रसायनिकी के प्रसार के लिए एक अद्वितीय मंच के रूप में विकसित हुई है। एनडब्ल्यूएमसी का प्राथमिक उद्देश्य शोधकर्ताओं को ऊर्जा, पर्यावरण एवं स्वास्थ्य के लिए पदार्थ के अनुसंधान क्षेत्रों से चुने गए विषयों पर मूलभूत सिद्धांतों के साथ-साथ संसामयिक एवं आधुनिक शोध से अवगत कराना है।

एनडब्ल्यूएमसी कार्यशाला श्रृंखला व्यापक रूप से लोकप्रिय है, जो विभिन्न संस्थानों के प्रतिभागियों की बड़ी संख्या से भली भाँति परिलक्षित होती है। इस वर्ष भी इस कार्यशाला के लिए लगभग 250 प्रतिभागियों ने पंजीकरण कराया है। "सिन-मैट" का उद्देश्य पदार्थ रसायनज्ञों को कार्यात्मक पदार्थों की रचना और संश्लेषित करने के लिए उपलब्ध संश्लेषण विधियों का सिंहावलोकन देना है। कार्यशाला का विचार-विमर्श पदार्थ रसायनिकी के क्षेत्र में समकालीन और पारंपरिक संश्लेषण ज्ञान पर ध्यान केंद्रित करेगा और इसमें पारंपरिक संश्लेषण विधियों, असम्यावस्था संश्लेषण विधियों, चिमी-डूस संश्लेषण, मेटाथिसिस, हरित संश्लेषण, आणविक और मृदुपदार्थों के संश्लेषण, उच्च दबाव पर संश्लेषण जैसे विषयों पर व्याख्यान शामिल होंगे।

पदार्थ रसायनिकी पर राष्ट्रीय कार्यशाला (एनडब्ल्यूएमसी), रसायनिकी प्रभाग, भाभा परमाणु अनुसंधान केंद्र एवं पदार्थ रसायनिकी संस्था, मुंबई द्वारा आयोजित की जाती है। रसायनिकी प्रभाग, भाभा परमाणु अनुसंधान केंद्र के सबसे पुराने प्रभागों में से एक है, जो भारतीय परमाणु ऊर्जा कार्यक्रम के प्रारंभिक चरण में अस्तित्व में आया था। प्रभाग ने परमाणु ऊर्जा विभाग के कार्यक्रमों से संबंधित अनुसंधान एवं विकास गतिविधियों को संचालित और विस्तारित करने का काम किया है। परमाणु ऊर्जा विभाग की जरूरतों को पूरा करने के अतिरिक्त, अग्रणी और उभरते अनुसंधान कार्यक्रमों को समायोजित करने के लिए रसायनिकी प्रभाग की गतिविधियों में भी समय के साथ कई बदलाव हुए हैं। रसायनिकी प्रभाग की कुछ प्रमुख गतिविधियों में परमाणु ऊर्जा कार्यक्रम से संबंधित नाभिकीय पदार्थ, हाइड्रोजन उत्पादन, भंडारण और शमन के लिए प्रयुक्त पदार्थों, ऊष्मा गतिकीय अध्ययन, ऊर्जा भंडारण के लिए प्रयुक्त पदार्थों, नैदानिक और चिकित्सीय पदार्थों, कार्बधात्विक पदार्थों, संसूचक पदार्थों, उच्च शुद्धता पदार्थों और संगणनात्मक रसायन विज्ञान पर अनुसंधान शामिल है।

पदार्थ रसायनिकी संस्था (एसएमसी) की स्थापना वर्ष 2007 में की गई थी एवं रसायनिकी प्रभाग, भाभा परमाणु अनुसंधान केंद्र को इसका मुख्यालय रखा गया था । संस्था का उद्देश्य भाभा परमाणु अनुसंधान केंद्र की सीमाओं से परे वैज्ञानिक संवाद को बढ़ावा देना है। संस्था अपनी स्थापना के बाद से आकार और लोकप्रियता दोनों में ही आगे बढ़ी है, जैसा कि इसकी वर्तमान आजीवन सदस्यता (लगभग 1950) से स्पष्ट है। एनडब्ल्यूएमसी श्रृंखला के

अलावा यह संस्था, द्विवार्षिक पदार्थ रसायनिकी पर अंतर वैषयिक संगोष्ठी श्रृंखला, उभरते विषयों पर प्रख्यात वैज्ञानिकों द्वारा विशेष व्याख्यान इत्यादि भी आयोजित करती है। संस्था (एसएमसी) अपना वार्षिक स्थापना दिवस, एक अतिविशेष व्याख्यान के आयोजन के द्वारा मानती है जिसमें एक प्रतिष्ठित वैज्ञानिक / प्रौद्योगिकीविद् को वैज्ञानिक समुदाय के साथ अपने अनुभव और ज्ञान को साझा करने के लिए आमंत्रित किया जाता है। वार्षिक स्थापना दिवस व्याख्यान को वर्ष 2022 में शुरू किया गया था। संस्था(एसएमसी) विभिन्न विषयों पर आलेखों वाले एसएमसी बुलेटिन का प्रकाशन भी नियमित रूप से करती रही है।

एनडब्ल्यूएमसी की आयोजन समिति, राष्ट्रीय सलाहकार समिति के सदस्यों का उनके अमूल्य मार्गदर्शन के लिए आभारी है। हम सभी संकाय सदस्यों, अनुसंधान विद्वानों एवं छात्रों को भी, एन डब्ल्यू एमसी-2023 में उनकी सक्रिय भागीदारी और रुचि के लिए धन्यवाद देते हैं। हम सत्र अध्यक्षों और आमंत्रित वक्ताओं का उनके समर्थन के लिए धन्यवाद व्यक्त करते हैं। आयोजन समिति वित्तीय सहायता के लिए नाभिकीय विज्ञान अनुसंधान बोर्ड (बीआरएनएस) की भी आभारी है। इस कार्यक्रम के आयोजन में रसायनिकी प्रभाग के वैज्ञानिक, तकनीकी और अन्य कर्मचारी गण द्वारा दिए गए निरंतर समर्थन और सहयोग हेतु हार्दिक आभार प्रेषित है।

हम एनडब्ल्यूएमसी-2023 में अपने सभी प्रतिभागियों के सुखद, परस्पर संवादात्मक और वैज्ञानिक रूप से लाभप्रद अनुभव की कामना करते हैं।

डॉ. ए.के. त्यागी   **डॉ. विनीता ग्रोवर गुप्ता**
(अध्यक्ष, एनडब्ल्यूएमसी - 2023)   (संयोजक, एनडब्ल्यूएमसी - 2023)

Preface

We welcome all participants to the prestigious DAE-BRNS 6th National Workshop on Materials Chemistry (NWMC-2023), which is a part of biennial workshop series organised by Chemistry Division, BARC in association with the Society for Materials Chemistry, Mumbai. The theme for this year's workshop is "Synthesis strategies of materials" also abbreviated as "Syn-Mat". The NWMC series was launched in 2011 as the first "DAE-BRNS National Workshop on Materials Chemistry (NWMC)" and has continued biennially thereafter. Since its inception, the NWMC series has received tremendous response from young researchers across the country and has evolved into a unique platform for dissemination of useful and fundamental materials chemistry knowledge along with discussion on forefront areas. The primary objective of NWMC has been to apprise the researchers with fundamentals as well as cutting edge research on the chosen theme from the research areas of materials for energy, environment and health.

NWMC series of workshop is widely popular, which is well reflected from the large number of participants from various institutions. This year as well, about 250 participants have registered for this event. "Syn-Mat" specifically aims at giving an overview of bouquet of synthesis strategies available to materials chemists to design and synthesize functional materials. The deliberations shall focus on contemporary and conventional synthesis knowledge in the field of materials chemistry and would include lectures on topics such as conventional synthesis strategies, non-equilibrium synthesis strategies, *chimie-douce* synthesis, metathesis, green synthesis, synthesis of molecular materials and soft matter, high pressure synthesis to name a few.

NWMC series of workshop is organised by Chemistry Division, BARC in association with the SMC. *Chemistry Division* is one of the oldest Divisions, which came into being at the early stages of the Indian Atomic Energy programme. The Division has served to nucleate and expand research and development activities relevant to the programmes of atomic energy. As several of these programmes blossomed with time, the divisional activities also underwent several changes to accommodate forefront and emerging research programs in addition to catering to department needs. Some of the key activities in Chemistry Division includes research on nuclear materials, materials for hydrogen generation, storage and mitigation, thermodynamic studies, materials for energy storage, diagnostic and therapeutic materials, organometallics, sensors, high purity materials and computational chemistry.

The *Society of Materials Chemistry* (SMC) was founded in 2007 with Chemistry Division, BARC as its head quarter for promoting scientific interactions beyond the institute's boundaries. The Society has grown since its inception both in stature and popularity as is evident from the current life membership of about 1950. Besides the NWMC series, SMC also organizes series of Interdisciplinary Symposium on Materials Chemistry (ISMC) every even year with special lectures on emerging subject areas by eminent scientists. The society arranges SMC Foundation day lecture that was started in 2022 where in an eminent scientist/technologist is invited to share his experience and words of wisdom with scientific community. The Society also continues to publish SMC Bulletins containing articles under different themes.

The organizing committee of NWMC, is grateful to the National Advisory Committee members for their invaluable guidance. We also thank all faculty members, research scholars and students for their active participation and interest in NWMC-2023. We express our thanks to session chairpersons and invited speakers for their support. The organizing committee is grateful to the Board of Research in Nuclear Sciences (BRNS) for financial assistance. Sustained support and cooperation extended by

scientific, technical and other staff members of Chemistry Division in organizing this event is sincerely acknowledged.

We wish all our participants a pleasant, interactive and scientifically rewarding experience at NWMC-2023.

Dr. A. K. Tyagi
(Chairman, NWMC-2023)

Dr. Vinita Grover Gupta
(Convener, NWMC-2023)

R & D Activities of Chemistry Division, BARC

Chemical science has played a prominent role in shaping India's indigenous nuclear energy programme. This has led to the initiation of chemistry activities in the Indian Atomic Energy Commission way back in 1949. Currently, Chemistry Group encompasses five divisions; namely, Analytical Chemistry Division, Chemistry Division, National Centre for Compositional Characterisation of Materials (at Hyderabad), Radiation and Photochemistry Division and Water and Steam Chemistry Division (at BARC-Facilities, Kalpakkam). Chemistry Division is the oldest Division of Chemistry Group. Its mandate has been to undertake both fundamental and applied research in thrust areas of DAE's vision programme. The major R & D activities of the Division are: Development of materials for nuclear energy, hydrogen energy, catalysis, healthcare, bio-sensors, high-purity materials, functional materials, toxic gas sensors & detectors, development of theoretical methods, computational chemistry, etc.

R & D in the area of nuclear materials primarily focuses on evaluation of thermo-physical and chemical properties of materials relevant to nuclear fuel cycles. Some of the activities in this area include research in sacrificial core catcher materials, materials for immobilization of actinides or lanthanides, as well as radiation stabile materials. Useful thermodynamic and thermo-physical properties generated on molten salts have a direct relevance to the development of Molten Salt Breeder Reactors (MSBR). Physico-chemical properties like heat capacity, thermal conductivity, water absorption-desorption and crush strength of the sintered red-mud bricks have been evaluated for application as sacrificial core catcher material. A stable crystalline complex phosphate has been prepared by an optimized solid-state reaction method, which can hold Cs^+ (~36 wt. %) up to its melting point. Structure and stability of iron phosphate glass (IPG) matrices containing Sb and Te have been evaluated. Superior glass forming ability and glass stability observed, which suggests IPG as an immobilization matrix of Sb and Te. Phase behavior of binary alloys in zirconium-iron (Zr-Fe) system and Zircaloy-steel system has been investigated to develop metallic matrix for immobilization of zirconium-based metallic nuclear waste originating from thermal nuclear reactors.

The Division also has made important contributions in the area of hydrogen generation, development of hydrogen storage materials, component materials for intermediate temperature solid oxide fuel cells and catalysts for mitigation of hydrogen in nuclear power plants under severe accident conditions etc. Ti_2CrV alloy samples were prepared for deployment in the bench scale hydrogen storage device of integrated hydrogen production and storage test facility. The alloys were characterized by EDS & XRD to confirm uniformity in composition & microstructure. The alloy has been tested for 50 hydrogen absorption-desorption cycles. Neutron diffraction study of the deuterated alloy reveals that D atoms occupy only the tetrahedral sites of the FCC lattice of the deuteride. D atoms are double in occupancy as compared to cations indicating a D/M value > 2 which matches well with the hydrogen uptake value of the alloy by gas sorption method. Research efforts have been made to develop materials for high energy and power density, enhanced safety and low-cost lithium and sodium ion battery (LIB and SIB). Mo_2C nanoparticles dispersed over rGO electrode have been prepared and evaluated for use in SIB. The unique design of $Mo_2C/C/rGO$ nanosheets exhibits specific capacity of 498 mAh/g at 50 mA/g current density against sodium electrode.

Under the affordable healthcare research program, efforts are being made for the development of nanodrug delivery systems for anticancer drugs, nutraceuticals, etc. Hyperthermia using magnetic nanoparticles (MNPs) has been introduced clinically as an alternative approach for local treatment of tumors. The surface engineering of MNPs with bioactive molecules is extremely important for their design and subsequent application in hyperthermia. In this aspect, protein conjugated glutaric acid functionalized magnetic nanoparticles were developed for hyperthermia therapy. The prepared MNPs are biocompatible towards normal cells and showed substantial cellular internalization in cancerous cells,

suggesting their potential application in hyperthermia therapy. Nanocrystalline materials emitting a single band red light under Near Infrared excitation has advantages in terms of cellular imaging in biological windows, as agents for photodynamic and photothermal therapy. Highly monodispersed upconversion nanocrystals functionalised with folic acid for targeting to tumor cells were prepared and tested for cellular imaging, under UV light and NIR excitation.

Over the years, Theoretical Chemistry Section (TCS) of BARC, which became an integral part of Chemistry Division, has made significant contributions in cutting edge research in theoretical and computational modelling of materials at different length and time scales. The primary goal of TCS has been to provide an in-depth understanding and rationalization of the observed chemical phenomena and more importantly, to predict new materials with tailor-made properties through the development of new concepts and the use of available computational tools. TCS is also involved in multi-scale modeling of molecules, clusters and materials, which covers the microscopic, mesoscopic as well as macroscopic length scales, dealing with the electronic structure, atomistic theory and simulation and continuum descriptions respectively. Recent advancements in the state-of-the-art techniques such as machine learning and high-throughput screening techniques have also been under taken for designing materials for energy, environment and nano-bio technology.

The research activities pursued in diverse areas have been published in peer reviewed journals, scientific bulletins, BARC News Letter, etc. and has also yielded several frontline technologies. A few indigenous instruments were also developed for in-house R&D use. Chemistry Division has to its credit transfer of several technologies for commercialization. The Division is well-equipped with major instruments like XPS, powder XRD, High Temperature XRD, Rotating Anode XRD, Single Crystal XRD, Small Angle X-ray Scattering, multinuclear NMR, TG-DTA, SEM, AFM, etc. Chemistry Division is also actively participating in collaborative projects with other research groups in BARC/ DAE, Universities (both in India and abroad)/ National Institutes through BRNS schemes, DST, international collaborations etc. Many colleagues have been conferred with prestigious awards from scientific bodies and fellowships from science academies. I take this opportunity to compliment all the colleagues for their sustained excellence in diverse areas relevant to the departmental programmes and look forward in making greater strides in coming years.

(Dr. A. K. Tyagi)
Head, Chemistry Division &
Director, Chemistry Group,
Bhabha Atomic Research Centre

About the Society for Materials Chemistry (SMC)
(Reg. No. - Maharashtra, Mumbai/F38063/2009)
C/o Chemistry Division, BARC, Mumbai 400 085

Materials Chemistry plays a significant role in the development of novel materials for advanced applications. The Society for Materials Chemistry (SMC) is a professional scientific body established in the year 2007 with Chemistry Division, BARC as its headquarters. SMC strive to promote education, research, and applications of materials chemistry among scientists and engineers in India and abroad. It also serves as a linkage between university researchers and other national laboratories under the Department of Atomic Energy (DAE). Since its inception, SMC is actively involved in organizing international symposia (ISMC), national workshops (NWMC) and publication of periodic SMC Bulletins.

Chemical Sciences has been at the forefront of developing materials for advanced applications. Some of the notable areas in which materials chemistry has played a pivotal role includes nuclear materials, energy technologies, healthcare, polymer science, catalysis, nanotechnology etc. This has led to the amalgamation of Chemistry with other disciplines and blurring the traditional boundaries among Physicists, Biologists and Engineers. The quest for enhancing the quality of life and demand for tapping alternate energy sources, witnessed enormous growth in the development of new materials. The advent of nanomaterials has also brought the new concepts of size and shape dependent functionalities of materials. Likewise, the need for innovative materials has risen in Nuclear Technologies as well, in particular from the point of view of new generation reactors such as Advanced Heavy Water Reactor, Compact High Temperature Reactor, Molten Salt Reactors, Accelerator Driven sub-critical systems and Fast Reactors with shorter doubling time.

The idea of launching Society for Materials Chemistry first germinated during National Workshop on Materials Characterization (NWMC) organized by Chemistry Division, BARC in Sept, 2004. This was further strengthened during 1st DAE-BRNS International Symposium on Materials Chemistry (December, 2006) organized by Chemistry Division BARC. In the valedictory function of ISMC-2006, several delegates supported the need of such scientific interactions for augmenting materials chemistry research in India. With these initial efforts, SMC was founded in early 2008. We are happy to inform you that through our persistent efforts the "Society for Materials Chemistry (SMC)" has been registered under the Mumbai registration act. This society hopes to provide a common platform to young researchers and active scientists in the area of material chemistry to exchange their ideas, develop interdisciplinary collaborations and share costly instruments / techniques available at premier institutes. SMC is actively involved in organizing international symposia and workshops, under the flagship titles Interdisciplinary Symposium on Materials Chemistry (ISMC) and National Workshop on Materials Chemistry (NWMC). SMC is also engaged in the publication of periodic SMC Bulletins and arranges series of lectures on various contemporary topics by eminent scientists across the globe. SMC also supports other agencies/societies in co-organising various events. SMC has instituted various award schemes to recognize outstanding contributions made in the field of materials chemistry.

We are happy to let you know that the current life membership of the society has reached about 1950 mark, with active participation of researchers from different institutes of India and abroad. SMC

also encourages formation of local chapters to make its presence nationwide and broaden its activities. Pune, Jaipur, Bhubaneswar and Delhi Chapters have already started its activities. We do hope for further enrichment of the strength and activities of this society and look forward for your active participation to take the society to greater heights.

(Dr. P. A. Hassan)

Vice President, SMC

Advisory and Organizing Committees, NWMC-2023

National Advisory Committee

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Schedule for NWMC-2023

Day 1; October 13, 2023		
Session & Time	**Activity**	**Speakers**
9:30 to 9:45 h		**Inauguration of Workshop**
Session -1 9:45 to 10:35 h	**PL**	**Dr. A. K. Tyagi** *Synthesis of materials beyond the phase diagrams*
High Tea (10.35 to 11:00 h)		
Session-2 11.00 to 13:00 h	**IT-1**	**Dr. Vinita G Gupta** *Solid state synthesis of materials*
	IT -2	**Dr. Dimple P Dutta** *Hydrothermal, microwave and sonochemical synthesis of nanomaterials*
	IT -3	**Dr. Rakesh Shukla** *Gel-combustion synthesis*
	IT-4	**Dr. S. N. Achary** *Synthesis of materials under high pressure/ high temperature conditions*
Lunch (13:00 to 14:00 h)		
Session-3 14:00 to 16:00 h	**IT -5**	**Dr. Sulekha Mukhopadhyay** *Chemistry at engineering Scale*
	IT-6	**Dr. R. K. Lenka** *Sintering of ceramics*
	IT-7	**Prof. Tapas K. Mandal** *Chimie-Douce approaches in the synthesis of novel inorganic solids*
	IT-8	**Dr. R. D. Purohit** *Flow control refractories for steel casting: role of materials chemistry*
Tea (16:00 to 16:30 h)		
16:30 to 17:30 h		**Ask me anything** *(Theme: Future of Materials and Career Prospects for Young Researchers)* **(Panelists: Dr. A. K. Tyagi, Prof. U. Kamachi Mudali, Dr. P. A. Hassan)**
Tea (17:30 to 18:00 h)		
18:00 to 19:30 h		**Annual general body meeting and award distribution function**
Dinner (20:00 to 21:00 h)		
Day 2, October 14, 2023		
Session & Time	**Activity**	**Speakers**
Session-4 09:30 to 11:00 h	**IT -9**	**Dr. P. A. Hassan** *Soft matter assisted synthesis of advanced healthcare materials*
	IT-10	**Dr. R. Mishra** *Phase diagrams for material synthesis*
	IT-11	**Dr. Adish Tyagi** *Molecular precursor mediated synthesis of nano-sized materials*
Tea (11:00 to 11:15 h)		
Session-5 11:15 to 13:15 h	**IT-12**	**Prof. Pushpal Ghosh** *Synthesis via ionic liquids: A green route to sustainable materials*
	IT-13	**Dr. Dheeraj Jain** *Metallic alloys and intermetallics: Synthesis methodologies*
	IT-14	**Dr. Raghumani Singh Ningthoujam** *Synthesis, characterization and properties of borides, carbides, nitrides and phosphides*
	IT-15	**Prof. K. Ramanujam** *Electro-valorization to synthesize value-added chemicals*
Lunch (13:15 to 14:15 h)		

Session-6 14:15 to 16:15 h	**IT-16**	**Dr. K. Bhattacharya** *Synthesis of low dimensional materials:A tale of different synthetic techniques*
	IT-17	**Dr. Mahesh Sunderarajan** *"AI/ML based design and synthesis of materials" Guiding experiments through quantum chemical GPS*
	IT-18	**Dr. Juby Kuttan** *Synthesis strategies for smart polymeric materials*
	IT-19	**Dr. Priyanka Ruz** *Soft chemical synthesis of functional micro-nano structures*
Tea (16:15 to 16:30 h)		
Session-7 16:30 to 17:30 h	**Quiz and Valedictory** **(Moderators: Dr. B. P. Mandal, Dr. Seemita Banerjee, Dr. Deepak Tyagi)**	

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Plenary Lecture

Synthesis of materials beyond the phase diagrams

A. K. Tyagi

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Abstract

The phase diagram concepts are widely used to prepare materials for various applications. This approach has its own merits; however, it has some limitations also. Often, it is not possible to prepare materials with unusual structure and in turn properties using the phase diagram-based synthesis protocols, which in general lead to thermodynamically stable and equilibrium compounds. The materials which are not formed under equilibrium conditions are classed as metastable materials. Often such metastable materials show exotic or extraordinary properties and hence they have great interest from both fundamental understanding or technological application points of view. This talk is intended to discuss synthesis of such unusual materials by innovative-yet-simple methods.

Phase diagrams enabled synthesis

Phase diagram is an essential tool to understand and predict the behavior of materials under different temperature and pressure conditions. This also provides the information on phases at different composition and also behavior of phase(s) at different temperature and/or pressure. Thus, the phase diagram helps to identify the stable phases of a material system at different temperature and pressure conditions. The information present in phase diagram provides crucial knowledge for selecting the appropriate conditions for material synthesis and also appropriate temperature limits for application. Phase diagram also provides information on phase transition and their natures, and that helps to understand the modes to control the phase transitions in desired direction. Thus, appropriate control on temperature and pressure across the phase boundaries can achieve necessary phase changes for producing desired material or to induce desired properties in a material. For example, control on phase transformation can be achieved through annealing, quenching and tempering, and they are mostly guided by the information in phase diagrams. In the synthesis of composite materials or in processes involving solute atoms in a solvent matrix, phase diagrams help to control solubility and precipitation behaviors. Thus, phase diagram guides to manipulate cooling rate, annealing or other heat treatment conditions to yield specific grain sizes, precipitate distributions, and phase combinations for optimized material for the desired properties.

Phase diagrams have been routinely used for designing alloys, solid solutions and compounds as well as composites with specific properties. It also guides to use equilibrium or non-equilibrium conditions to control composition, defects and microstructure in single phase or multiphases materials, which is often used to develop alloys and composites with better properties. For materials such as semiconductors and ceramics, phase diagrams help control the formation of defects like vacancies, interstitials, and grain boundaries. By adjusting the synthesis parameters based on phase diagrams, one can minimize or control defect formation, leading to improved material performance. By comparison of phase diagrams of different systems, it is possible to choose the most suitable materials based on stability, compatibility with other materials, and performance under specific conditions. The phase diagrams provide valuable insights into high-temperature stability of materials of interest. Phase diagram guided manipulation of cooling rate, annealing, or other heat treatment processes can yield specific grain sizes, precipitate distributions, and phase combinations that optimize material properties. Thus, it is amply clear that phase diagram concepts will never be outdated as they will continue to provide broad guidelines in the field of materials science

Limitations of phase diagram enabled synthesis

The phase diagrams are constructed under thermodynamic equilibrium conditions which imply that it will lead to materials corresponding to global free energy minima in the free energy landscape. Hence, the major limitation of phase diagrams enabled synthesis is that it does not result in materials which exist under non-equilibrium conditions, in particular metastable materials. Metastable state is a non-equilibrium or quasi-equilibrium state which may persist for long time under suitable conditions. The origin of metastability in materials is due to the trapping of materials in a local minimum in the potential energy curve. A typical case is of glasses which exist in reality, but do not exist in equilibrium phase diagrams. Phase diagrams provide information on the possible glass forming compositions but not the conditions to attain them. Thus, they need a method beyond the conventional process of phase diagram. Similarly, a wide variety of composition and structures exist even in crystalline materials which are not the equilibrium condition phases of conventional phase diagram. Phase diagram provide only limited or no information on such phases. A number of phases occur only at high temperature in phase diagram, but they either transform to different phases or decompose to different components when they are brought back to ambient conditions. A number of non-equilibrium process or modified synthesis strategies are desired to retain such materials at ambient conditions. A simplest case can be mentioned here as stabilization of cubic ZrO_2 by decreasing the crystallize size below a critical size (about 8 nm), or by doping suitable lower valent cations, like Y^{3+}, Ca^{2+}, etc. In addition, there can be a crystalline material with unusual structural arrangements, viz. abnormally short or long bonds; exceptionally lower or higher packing efficiency, unusual coordination numbers or oxidation states. Such materials are termed as crystallographically metastable state material. Phase diagram also remain as less importance for synthesis of such materials, as they involve multiple parameters for their formation and sometimes antagonistic parameters for their existence. Such crystallographically and chemically metastable materials exhibit different physical properties, like transport, optical and magnetic and catalytic properties.

Often exotic structures and properties have been often encountered in such metastable materials compared to their analogous stable state and thus such materials become more attractive from fundamental understanding and technological applications. Many exciting materials are metastable. Such materials are mostly obtained under non-equilibrium thermodynamic conditions by using non-conventional and soft-chemical preparation methods. Thus, the syntheses of such materials have been a challenge and in turn provide opportunities to chemists.

Synthesis of unusual materials

In my group, a number of new functional metastable materials have been prepared by using non-equilibrium processes, viz. combustion method, heating under very low partial pressure of oxygen, high pressure synthesis, intercalation/ deintercalation processes, ion-exchange method etc. The synthesis of these materials with desired properties requires novel routes that can take place at milder conditions. Some of these methods are described as follows:

Solid state metathesis (SSM) reaction is one of the methods in which reaction among metal halides/nitrates with other group compounds in very fast, exothermically, leading to a crystalline product and soluble metal halide/nitrate salt as a by-product. SSM reactions provide better synthetic control over product crystallinity, phase purity and microstructure. Several stable and metastable compounds like oxides, phosphides, sulfides, nitrides and silicides have been synthesized using this method. Sometime such methods also involve several reactive or metastable species as intermediate phase or precursors, and that help to control over the product in terms of stoichiometry, crystallite size and microstructure.

Synthesis of materials by ion-exchange is one such low temperature preparative route that can be utilised to design rational synthesis to obtain materials with desired structures and morphologies. Ion exchange is defined as the reaction in which the exchangeable or the free mobile ions of one solid can be exchanged for different ions with different materials which could be solid, liquid or gas. The

ions that are being exchanged may have similar or different charges also. Structurally, to facilitate the exchange, the exchanger must have relatively open network structure that should be able to carry the ions and allow them to pass through it. It has become a technique of choice to synthesize novel three-dimensional layered structures that possess exchangeable cations. It has been used to synthesize nano-materials, not just *de novo,* but also as a *post-synthetic* procedure to obtain hitherto inaccessible phases and complex hetero-structures which have applications as next generation catalysts, electrical, optical, opto-electronic and magnetic materials. This method is capable of producing materials with unusual structures and coordination numbers.

Another very interesting method is based on intercalation or deintercalation, which often leads to materials beyond phase diagrams. In this method, first a stable material based on phase diagram is prepared. Subsequently, some of the cations or anions are gently intercalated or deintercalated to form materials which otherwise do not exists in phase diagrams. In my group, several metastable materials have been synthesised by this novel method. A few representative examples will be discussed in this talk.

The concepts of counter cation or anion facilitate synthesis of many unusual materials. In this particular approach, counter ions with appropriate size, electro-positivity or electro-negativity, polarisability are selected to prepare unusual materials. For examples, often highly electropositive counter cations are able to stabilise other cations in unusually high oxidation state. Typical examples are $BaFeO_4$, $BaCrO_4$, $KCuO_2$ and $KBiO_3$ etc. Likewise, it is possible to stabilise low oxidation state metals by taking an anion with high polarisability. For example, some of the divalent lanthanide ions can be easily stabilised in iodide form. Some of the examples will be discussed.

Preparative chemistry under high pressure has become an interesting and challenging process for the preparation of novel functional materials, where the common crystallographic and thermodynamics constraints can be easily deviated. Thus, the reaction of materials under high pressure and temperature can lead to newer products which otherwise cannot be obtained by the conventional high temperature reactions. The introduction of pressure alters the conventional temperature induced reaction pathways and in turn a different pathway is adopted. Usually, application of pressure increases the repulsive forces between the bonded atoms, as well as increases attractive forces for non-bonded atoms. The increasing attractive forces between non bonded atoms may bring them to bonding state and hence, un-usually higher coordination number and higher packing density are achieved and that in turn is reflected in their electronic properties also. Some of the examples of such studies will also be discussed. There are examples when lone pair becomes a bond pair under high pressure which leads to exotic compounds with unusual properties.

Conclusions

Though the phase diagram provides information on the existence and formation conditions of a phase under equilibrium conditions, often the phases formed under non-equilibrium conditions remain elusive. This presentation will provide an overview of wide varieties of methods being used to prepare metastable materials, which otherwise are not existing under normal ambient condition as per the phase diagram. Several types of techniques, like combustion method, controlled atmosphere, high pressure synthesis, intercalation / deintercalation processes, ion-exchange method etc. used to prepare such non-conventional materials will be briefed upon.

Dr. A. K. Tyagi joined Chemistry Division, BARC in 1986 through BARC Training School. He obtained PhD in 1992. He did postdoctoral research at Max-Planck Institute, Stuttgart, Germany (1995-96). Presently he is Director, Chemistry Group, BARC, Distinguished Scientist, DAE and Senior Professor (Chemistry) at Homi Bhabha National Institute (HBNI), Mumbai and honorary Professor at JNCASR, Bengaluru. His research interests are in the field of nanomaterials, functional materials, nuclear materials, metastable materials and hybrid materials. He has published more than 650 papers in international journals, 11 books and several review articles. He has supervised 35 students for their PhD and another 08 students are presently pursuing PhD under his supervision. He is presently Chairman, BARC Standing Academic Committee (Chemical Science and Biological Science).

He has been conferred with a number of prestigious awards such as such as DAE-Homi Bhabha Science and Technology Award, DAE-SRC Outstanding Researcher Award, DAE-Group Achievement Award; MRSI Medal; MRSI-ICSC Materials Science Senior Award; MRSI-CNR Rao Prize in Advanced Materials; CRSI Bronze Medal; CRSI-CNR Rao National Prize in Chemical Sciences; CRSI-Silver Medal; Medal of Indian Nuclear Society; Rheometric-ITAS Award; ISCAS-Dr. Lakshmi Award; IANCAS-Dr. Tarun Datta Memorial Award; R. D. Desai Memorial Award of Indian Chemical Society; Rajib Goyal Prize in Chemical Sciences; ISCB Excellence Award in Chemical Sciences; CCRS Award in Chemical Sciences; ISCA Platinum Jubilee Lecture Award in Materials Science; Metallurgist of the Year award from Ministry of Steel, GoI; JNCASR-National Prize in Solid State and Materials Chemistry; ISCA Acharya PC Ray Memorial Award; NASI – Prof. N.R. Dhar Memorial Award; JNCASR-Prof. AV Rama Rao Foundation Lecture Award; and NETZSCH – ITAS Award by Indian Thermal Analysis Society.

He is a Fellow of all the major science academies in India such as the Maharashtra Academy of Sciences; National Academy of Sciences, India; Indian Academy of Sciences; Indian National Academy of Engineering and Indian National Science Academy. He is a Fellow of several international science academies also such as Royal Society of Chemistry; Asia Pacific Academy of Materials; World Academy of Ceramics and African Academy of Sciences.

He has been a visiting scientist to several countries like USA, France, Canada, Japan, Russia, Germany, China, Portugal, Singapore, Australia, Sweden, Italy, Spain, Israel, Malaysia and South Africa.

Invited Talks

Solid state synthesis of materials

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Advancement in materials has always been an important marker for growth and development of the society. In today's times, when the risk of running out of conventional energy resources is looming large along with the irreversible climate change that has been brought about by alarming increase in greenhouse gases, discovery of materials that could contribute towards sustainable development goals in particular the energy security and net zero goal has become paramount. And with this the synthesis of new, advanced and better materials by a synthesis route that can ensure scalability has become absolutely essential.

This lecture will focus on the synthesis of inorganic materials by *solid state synthesis*. It is an important route for syntheses of novel compounds, materials, and high-temperature phases. It has been conventionally used to synthesize various classes of functional materials such as materials for energy applications, optical applications (luminescent materials, pigments), materials for electrical applications (ionic conductors, ferroelectrics, superconductors) etc. There are various high temperature routes and their variations that are available to scientists to synthesize new materials. Some of them include:

1. Basic ceramic method or the solid state synthesis method
2. Spark plasma assisted solid state synthesis
3. Microwave assisted solid state synthesis
4. Co-precipitation followed by heating
5. Flux synthesis

Basic Solid State Synthesis (or the Ceramic Synthesis Route)

Solid state synthesis is probably one of the oldest and the simplest preparative methods followed worldwide. In the simplest terms, it involves mixing the components and heating them together at some higher temperature for a particular duration of time to get the desired product. It is also one of the most favored method of synthesis for bulk production because of the simplicity of the preparative procedures. It can be used to prepare an extremely large number of compounds including metal oxides, sulfides, carbides, silicates etc. It is basically taking two non-volatile solids together in desired proportions, mixing them up and firing them at high temperatures. Solid state synthesis is generally a multi-step process and the basic steps involved in solid state synthesis are:

1. Judiciously selecting the reactants
2. Weighing them in appropriate proportions
3. Mixing/ grinding them either by ball mill or using mortar-pestle
4. Preparing the pellets and heating at high temperature and appropriate atmosphere.
5. Repeating step 3-5 till desired single-phasic product is obtained.

e.g. Synthesis of zircon, $ZrSiO_4$ can be done by using ZrO_2 and SiO_2 as the reactants. The individual reactants are weighed, mixed and pelletized followed by heating at high temperature (1200 – 1300 °C) as given by the reaction:

$$ZrO_2 \text{ (s)} + SiO_2 \text{ (s)} \longrightarrow ZrSiO_4 \text{ (s)}$$
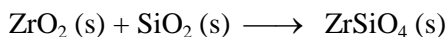
It may appear a trivial procedure, but there are several factors that need to be taken care of before planning a successful synthesis. Some important factors are temperature, area of contact, duration of heating, nature of reactants and reaction atmosphere. Many of these factors can be easily understood considering that solid state reactions are the diffusion-controlled reactions. Various factors that affect solid state synthesis and need to be controlled are:

1. *Temperature:*

The temperature chosen for the solid-state synthesis depends largely on the melting points of the reactants. e.g. synthesis of solid solutions of rare earth fluorides such as a mixed phase of NdF_3 and MF_2 (M: Ca, Sr, Ba) will require the temperature of ~900°C whereas synthesis of the solid solutions of rare earth oxides will need temperatures ~ 1300°C - 1500°C. This is because the fluorides have lower melting points as compared to oxides. Lower melting points translates to better mobility of ions at lower temperature which lead to better extent of reactions at temperatures lower than those required for oxides. In addition, reaction between lower melting solid will also require lesser number of steps. An approximation of synthesis temperature is given by Tamman's rule. *It suggests that temperature of about two-thirds of the melting point (K) of the lower melting reactant is needed to be maintained for the reaction to occur in a reasonable time.* Also, the reactivity of solids increases considerably in the vicinity of phase transition, this concept is known as the Hedvall effect. The heating and cooling rates of the solid state reaction are also an important parameter.

2. *Area of contact:*

Because the solid-state synthesis is governed by diffusion, the homogeneous mixture of reactants as well as the area of contact between the reactants also play an important role. The higher area of contact translates into better diffusion and is controlled by thoroughly grinding the reactants together either by hand or by ball-milling. Better area of contact may also be ensured by choosing the starting reactants in the nano-form. This increase the interparticle contact area as well as lessens the diffusion distance. Pelletising the homogeneously mixed powders in the hydraulic press also maximizes the area of contact between the crystallites. The gradual thickening of product layer prevents the diffusion of the reactants and that is the reason most of the solid state syntheses require multistep heating with "repeated intermittent grindings".

3. *Reaction atmosphere:*

The selection of proper atmosphere during the reaction is also crucial for obtaining desired compounds. Different types of atmospheres such as static air, flowing air, flowing oxygen, inert atmosphere (argon,), reducing atmosphere etc. can be used depending on the nature of reactants as well as the oxidation states of the reacting species/ions desired in the end products.

4. *Miscellaneous factors:*

A low temperature pre-heat treatment of the reactants, before mixing up the reaction mixture, is always advisable before actual synthesis to remove water and adsorbed gases. In addition, if the reactants chosen are carbonates, acetates etc., the reaction mixture should be given a low temperature heat treatment to decompose them which has an additional advantage of higher surface area and the fast reaction due to *insitu* prepared oxides. Also, the heating rate and the material of reaction crucibles also should be chosen with a great care. The common crucible materials used are quartz, alumina, Pt, Au, Silver, etc. The crucibles made up of refractory oxides like YSZ are also used for very high temperatures ($\geq$ 2000°C).

Advantages of solid state route

The solid-state route is simple and an extremely versatile process, best suited especially for bulk production. Also, the advantages of solid-state reactions are the ready availability of starting oxide and the low cost for powder production on a large scale. These reactions are also convenient on laboratory scale.

Drawbacks of solid state route

A general drawback of the process is that the mixing and grinding may give rise to non-uniform composition and local stoichiometric variations. Also, long grinding duration can give rise to an increase in the contamination from the grinding media. Additionally, this process requires high temperatures and long annealing durations. This is because the proximity of the reacting species achieved in the solid-state synthesis is understandably rather inferior. As a result, the reacting species have to migrate over larger distance in the diffusion, hence requiring higher temperature resulting in products that are coarse in nature. These types of products are sometimes difficult to process and are not suitable for applications wherein the shaping of the product is required.

Variations of solid state synthesis route based on heating source

In general, in the conventional solid state synthesis, the reaction mixtures are heated at high temperatures in the furnaces which are heated by heating elements wherein the electrical energy is converted into heat. The details of various types of furnaces and heating elements would also be discussed in the lecture. However, the energy can be provided to the reactants by other sources as well and this leads to variations of conventional solid state heating method. Some examples are discussed below.

1.   Microwave solid state synthesis

The reaction time can be diminished if one of the major reactants is a microwave (MW) absorber. MWs have wavelengths between 0.01 and 1 m, however, the frequencies allocated for scientific use are 900 MHz and 2.45 GHz. Under microwave irradiation, reactions can be accelerated owing to rapid heating, selective coupling and also enhanced reaction kinetics and there is minimal energy loss along with uniform heating. It can also lead to structurally and/or chemically different reaction products. Another advantage is extremely rapid temperature rises, and if required, immediate stoppage of heating leading to fast quenching. This may yield metastable products which are generally unachievable by conventional solid state synthesis. In addition since, it also cause selective heating of the reactants, it makes possible the synthesis of materials wherein one reactant is volatile. The temperature rise is observed in the non-volatile reactant and the reaction is made feasible. E.g. It enables successful synthesis of metal chalcogenides which are difficult to synthesize conventionally due to the volatility of the chalcogen starting materials. Using MWs, the metal components of the reaction mixture are heated preferentially and react very quickly with the chalcogen before it has chance to volatilize. The talk shall discuss the mechanism of microwave synthesis alomg with suitable examples.

2.   Spark plasma assisted solid state synthesis

In this method of synthesis, the material is internally heated by Joule effect by pulsed direct current which leads to faster heating rates. A simultaneous application of additional uniaxial pressure allows for the contact between the grains of the reactants and lead to shorter reaction durations and also controls the grains growth. The spark plasma sintering method was conventionally developed for advanced sintering technique for consolidating nanopowders into nanostructured bulk materials. Since the powders in the

spark plasma setup experience the action of both pulsed electric current and uniaxial pressure; this leads them to be heated at very high rates which are almost unachievable in furnace heating and this causes them to be sintered within shorter times frames and at lower temperatures as compared to the conventional methods. However, the design of the facilities and the underlying principle has made it quite attractive for conducting solid state synthesis. Oxides such as Li_2CoPO_4F (battery material) [42] and Magnelli phases such as V_6O_{11} were synthesized by spark-plasma-sintering technique.

3. *Flux synthesis:*

Molten salt synthesis is one of the relatively low-temperature solid state synthesis routes which employs fluxes which are normally the low melting eutectics. The flux provides a medium for the reaction to occur fast by decreasing the diffusion distance and increasing the mobility of reactants. Generally, alkali chlorides, sulphates, carbonates and hydroxides are used as flux. The melting point of the flux must be lower than the formation temperature of the product. Also, the product must be easily separable from the flux after the reaction is over. In the flux synthesis, the reactants are mixed with flux and heated above the melting point of flux and after the reaction, the flux is washed out to obtain the products. The flux or the molten salt synthesis has been employed to obtain several technologically important materials like ferrites $BaFe_{12}O_9$ and $Pb(Zr_{1-x}Ti_x)O_3$. The powders obtained after the flux synthesis have better sinterability as compared to those obtained by solid state synthesis method.

4. *Co-precipitation Synthesis*

Co-precipitation provides a ready alternative to obtain atomistic level mixing of reactants to overcome the issues related to diffusion distance. This involves co-precipitating the reactant ions using a common precipitant to obtain a precursor which can then be further processed at high temperature to get desired products. It is an easy and energy efficient pathway that also brings down the synthesis temperature. However, there are certain criteria needed to be fulfilled such as comparable solubility of the reactants and their precipitation rates etc. These shall be discussed with suitable examples.

Summary

The development of mankind is governed by synthesis of new advance materials. In inorganic material synthesis, high temperature synthesis routes are the oldest and the most practiced synthesis routes which are easily amenable to scaling up. One needs to choose proper reactants, reaction temperature, reaction duration, atmosphere, reaction crucibles. Solid state high temperature synthesis yield thermodynamically stable product with preserved stoichiometry of the reactants. There a wide variation to high temperature solid state synthesis available which may reduce the reaction T and duration by yielding a well homogenized reaction precursor. The readers are advised to refer the books [mentioned in references] which deal extensively with experimental solid state chemistry. These will also enlighten the researchers about new directions in solid state chemistry.

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Hydrothermal, Microwave and Sonochemical Synthesis of Nanomaterials

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Introduction

Nanomaterials have emerged as an exciting class of materials that are in high demand for a range of practical applications. They have sizes in the range of 1 to 100 nm, at least in one dimension. Nanotechnology is an excellent example of an emerging technology, offering engineered nanomaterials with the great potential for producing products with substantially improved performances. The invention of various spectroscopic techniques sped up research and innovations in the field of nanotechnology. The physical and chemical properties of nanomaterials depend upon their precise composition, shape, and size. Hence, method of synthesis plays a crucial role in all aspects of nanotechnology. The inability of many processes to manufacture high-quality nanomaterials in a consistent and safe way is in part due to inherent limitations of processes or lack of knowledge on particle−parameter behaviors. For example, processes that involve very high temperatures such as flame, combustion, or plasma processes result in phase separation or extensive agglomeration with low surface areas. Some of these methods also produce highly charged NPs in the gas phase, which could potentially be hazardous to workers as they are airborne and present a potential inhalation hazard. More conventional NP synthesis methods such as sol−gel and coprecipitation techniques are slow, require multiple steps, and need very precise control of several reaction parameters (pH, temperature, etc.), otherwise yielding inconsistent products. Emulsion syntheses of NPs can be very wasteful, often requiring large amounts of organic solvents. Furthermore, ball milling (top down method) is energy intensive and slow and makes materials in a dry powder form, which could pose an inhalation hazard. Increasing the control, speed, and homogeneity of NP manufacturing methods will significantly enhance product quality and consistency of de novo engineered nanomaterials. Among the various bottom-up approach of synthesis of nanomaterials, hydrothermal/solvothermal, sonochemical and microwave assisted techniques are being pursued seriously. In this lecture, concepts related to these synthesis techniques and a few specific examples will be discussed in detail.

Hydrothermal and Solvothermal synthesis

The hydrothermal process is one of the most well-known and extensively used methods used to produce nanostructured materials. In the hydrothermal method, nanostructured materials are obtained through a heterogeneous reaction carried out in an aqueous medium at high pressure and temperature around the critical point in a sealed vessel. In the manufacture of high-quality homometallic or heterometallic oxide nanomaterials, hydrothermal processes offer significant benefits because they can operate at relatively low synthesis temperatures (as compared to flame and plasma processes) and follow cleaner processing routes, not involving organic solvents. In a typical hydrothermal process, water is heated above its boiling point under pressure to cause precipitation or crystallization of inorganic materials, akin to processes in which minerals are formed under the earth's crust over long periods or indeed in hydrothermal vents, which are deep under the sea. The solvothermal method is like the hydrothermal method. The only difference is that it is carried out in a non-aqueous medium. Hydrothermal and solvothermal methods are generally carried out in closed systems. Hydrothermal and solvothermal methods are exciting and useful methods for producing various nano-geometries of materials, such as nanowires, nanorods, nanosheets, and nanospheres.

Hydrothermal processing is an unconventional method to synthesize nanocrystalline inorganic materials. Direct precursor-product relation exists thereby allowing synthesis of roughly every material with no requirement of structure defining agents. It is well recognized that the majority of inorganic materials become soluble in water at high temperature and high pressure. Hydrothermal method is based on this premise wherein the materials are dissolved in water under high temperature

and pressure conditions. These dissolved substances are then crystallized to obtain the desired end products. Being indicated in the name, water performs a crucial role in precursor material transformation process at elevated temperatures. According to the phase diagram of water, merely the branch between gaseous and liquid state warrants further considerations: at less than 100 °C, equilibrium vapour pressure of water (liquid state) is <1 bar; and beyond the boiling point significant hydrothermal pressure range exists. Generally, two different operating modes can be identified. Hydrothermal processing is usually performed in a steel pressure vessel also defined as autoclave wherein the processing conditions are controlled by adjusting the temperatures and/or pressures. The autoclave may or may not be coated with protective Teflon coatings. The processing is carried out in aqueous solution. Temperature is increased beyond boiling temperature of water, attaining the pressure of vapour saturation. Internal pressure depends largely on temperature and the quantity of solution put in the reaction chamber (autoclave).

Hydrothermal synthesis is affected by the temperature and pressure below a critical point for the solvent. Some oxides are more soluble in the hydrothermal salt solutions in comparison to the pure water. These hydrothermal salts are termed as mineralizers. Furthermore, there exist solvothermal processing techniques which are analogous to the hydrothermal methods. The main difference betweenthe hydrothermal and solvothermal processes is that the latter uses organic solvents and supercritical carbon dioxide. Nanopowders can be synthesized by either:

a.   directly hydrolyzing the precursors in the autoclave at elevated temperatures. In this case, an aqueous solution containing the precursor is placed inside the autoclave, or
b.   room temperature hydrothermal processing of the reaction products. In second case the crystallization rate of amorphous phases rises abruptly under the hydrothermal processing conditions. In this case, the autoclave is loaded with a suspension of reaction products carried out at ambient.

In both cases, a temperature difference is not required to be maintained. Also, no specialized equipment is needed. The hydrothermal technique has a lot of other advantages like it accelerates interactions between solid and fluid species, phase pure and homogeneous materials can be achieved, reaction kinetics can be enhanced, the hydrothermal fluids offer higher diffusivity, lower viscosity, facilitate mass transport and higher dissolving power. Most important is that the chemical environment can be suitably tailored. Although the process involves slightly a longer reaction time compared to the vapour deposition processes, or milling, it provides highly crystalline particles with a better control over its size and shape.

Substantial enhancements in hydrothermal processing facilitate in controlling the reactions by usingexternal factors. For example, hydrothermal processing is being used in conjunction with microwave, ultrasonic, electrochemical and mechanochemical syntheses. The microwave-assisted hydrothermal method has recently received significant attention for engineering nanomaterials, combining the merits of both hydrothermal and microwave methods.

Zeolites (synthetic) are among the most frequently produced nanomaterials by using hydrothermal processing. Their growth strongly depends upon the presence of surface activation agents within the solution. These agents control the morphology of oxide products in hydrothermal solutions. The choice of synthesis conditions and type of surfactants can ensure the production of targeted porous nanomaterials with given pore size controlled in a wide range of values.

Microwave assisted synthesis

Microwave-assisted synthesis has seen rapid development in the last two decades as it is being heralded as a green synthesis technique. Microwaves are electromagnetic waves having frequency in the range of 0.3 - 300 GHz and are located between the infrared and radiofrequency region of the electromagnetic spectrum. The energy associated with the microwave radiation varies from 1.24×10^{-6} to 1.24×10^{-3} eV which is insufficient to break chemical bonds or even trigger Brownian

motion. The synthesis is based on the effective absorption of microwave energy by the reactants/solvents in a chemical reaction which results in efficient heat transfer through dielectric heating. The reactions occur at a must faster time scale compared to conventional thermal heating and helps in the reduction of carbon footprint. In order to avoid interference with cable communication and mobile phone frequencies, all domestic microwave ovens and dedicated microwave reactors for chemical synthesis, operate at a frequency of 2.45 GHz. Earlier, most of the chemical reactions were performed in household microwave ovens which had poor control over the experimental parameters and hence there was a reproducibility issue with the reported experiments. However, in recent times, microwave assisted synthesis has gained prominence with the availability of microwave reactors with special features like built-in magnetic stirrers and temperature and pressure sensors. Consequently, its application in material sciences, nanotechnology, organic/ peptide synthesis, polymer science, and biochemistry has gained immense prominence.

The heating effect of microwaves (MW) is triggered by mechanism of dipolar polarization and ionic conduction depending on the materials used for the reaction. When polar solvent or reagents are involved, the dipoles in the sample strive to align themselves in the direction of the applied electric field under influence of microwaves. Since the electric field oscillates, the molecular dipoles attempt to re-align themselves accordingly along the alternating electric-field and this leads to loss in energy through molecular friction, rotation and dielectric loss. The heating effect is related to the ability of these molecular dipoles to realign themselves with the applied field frequency. Heating effect is disrupted if the dipoles align too quickly which happens with low frequency radiation or if unable to reorient themselves which occurs when the frequency of MW radiation is high. In ionic conduction mechanism, as the name suggests, the ions formed in the solution, collides with the neighbouring atoms or molecules in the presence of the oscillating electric field and energy is lost in the form of heat. The heating effect through ionic conduction is stronger compared to that obtained via dipolar rotation mechanism [7]. This is evident when equal volume of distilled water and tap water is heated under identical radiation power and fixed time in a MW reactor. The final temperature is higher in the tap water sample containing dissolved ions as in this case both dipolar polarisation and conductive mechanisms contribute to the heating effect. The microwave heating effect of any material is expressed by its loss tangent/loss factor $\tan \delta = \delta''/\delta'$, where δ'' is the conversion efficiency of the electromagnetic radiation into heat (dielectric loss) and δ' is the polarizability of molecules in the electric field (dielectric constant). The angle δ represents the phase lag between the polarization of the material and the applied electric field and helps in determining the efficiency of the microwave heating process. The parameters which affect loss tangent are temperature and frequency and they also play a role in the penetration depth of MW radiation in any material. Penetration depth refers to the point in the material which retains 37% of the initial irradiation power.

It has been observed that microwave heating accelerates the rate of chemical reaction which reduces the reaction time considerably. Also, certain reactions which do not occur under conventional heating methods can be performed under identical condition via microwave heating.

The advantages of MW assisted synthesis are rapid uniform volumetric heating, higher chemical reaction rate and selectivity, shorter reaction time, higher product yield and green synthesis as compared to the conventional heating methods. This method leads to the formation of inorganic nanostructures in shorter time which results in low cost of production, energy savings and higher reaction efficiency. Various solvents with different MW absorbing power can be used for synthesis which can alter the chemical composition, size and morphology of the nanoparticles which have vast applications in the field of materials science. Hence, microwave heating technology is gradually gaining popularity for performing chemical reactions. Though considerable research has been done on this topic for the last two decades, the earlier reports are unreliable since most of the reactions were done using domestic microwave ovens where the conditions of the experiment were not standardized. The repeatability of such experiments and reproducibility of the results is thus dubious for these reports. Currently, the MW reactors have precise temperature and pressure monitoring by various probes and sensors, built-in magnetic stirring, power control, cooling system, and software operation which has increased the popularity of this technique.

Sonochemical Synthesis

Sonochemistry offers a simple route to nanomaterial synthesis with the application of ultrasound. The tiny acoustic bubbles, produced by the propagating sound wave, enclose an incredible facility where matter interact among at energy as high as 13 eV to spark extraordinary chemical reactions. Within each period – formation, growth and collapse of bubbles, lies a coherent phase of material formation. This effective yet highly localized method has facilitated synthesis of various chemical and biological compounds featuring unique morphology and intrinsic property. The benign processing lends to synthesis without any discrimination towards a certain group of material, or the substrates where they are grown. As a result, new and improved applications have evolved to reach out various field of science and technology and helped engineer new and better devices.

Ultrasound passing through a solution creates regions inside the solution with high- and low-pressure region according to the periodic compression and expansion. This change in pressure marks the inception of sonochemistry, as it precedes the crucial process of acoustic cavitation i.e. formation, growth and collapse of acoustic bubble. Air molecules dissolved in the solution diffuse to form bubbles at the low pressure cycle. On reaching the next cycle, the high external pressure compresses the bubble and the matter inside violently. This process of bubble growth and compression continues until the external pressure dominates and the bubble collapses. As they contract, the acoustic bubbles, with high energy particles inside, emit light (200–800 nm) for a very brief period (about 100 ps). This phenomenon, known as sono-luminescence, can be used to analyze the condition inside the acoustic bubble. With the help of such tools andtheories, pressure and temperature inside the bubble has been calculated to rise to more than 1000 atm. and 5000 K during cavitation. The core region, known as the hotspot, feature high-energy particle collision that generate energy as high as 13 eV. Extreme cases of ionization and formation of plasma inside the bubble have been reported with different chemicals and solvents. The utility of sonochemistry lies in the fact that the ions and radicals inside the bubble comes from the chemical solution; therefore, choosing appropriate chemicals based on their vapor pressure can help customize the overall process.

Sonochemistry strives to alleviate exactions and simplify material processing. Metal, polymer, protein, graphene, liquid-filled spheres and many such new and uncommon materials continue to unleash to offer new applications or improve existing ones. Use of sonochemistry is, however, not merely limited to processing of such nanomaterials, but also, in rendering them useful for improved applications. From catalysis, cleaning, sensing, solar energy harvesting to targeted drug delivery, diseasetreatment, body imaging etc., scope of sonochemistry expands overvarious fields of science and technology, and continues to be consistent with the current trend. Sonochemistry shows to not only avail contemporary research and processes, but in some instances, has proved to be a better technique than the conventional and matured ones. The opportunities sonochemistry sets up are as exciting as the process, and are imminently realizable. Understanding the mutual effect of input parameters can not only assure control over nanomaterial growth, but also help grow specific materials and unlocknew applications. Sonochemically synthesized catalytic metal nanoparticles used in purification, can be furthered to autonomously rectify waste and pollution. Precise drug delivery with the help of sonochemically synthesized protein microcapsules has shown encouraging result in case of tumor treatment, and with the active ongoing research can soon be applicable for other medical conditions. Similarly, the facile sonochemical processing of graphene, carbon nanotubes etc. can help achieve the immense potential these materials promise if performed in large scale. Sonochemistry reaches out even farther for its ability to use different substrates to grow such expedient materials. ZnO nanoparticles synthesized sonochemically on paper and fabrics such as cotton and nylon forecast the advancing smart textile industry. The effective antimicrobial property of ZnO and its UV screening, given its biocompatibility, will not only help improve our health standard but also the textiles we use in daily basis.

Conclusion

Apart from the above conventional synthesis of nanomaterials, certain advanced methods will be also introduced to the participants. These include continuous hydrothermal flow synthesis (CHFS) processes, microwave-assisted hydrothermal and microwave-assisted sonochemical techniques. In the last decade, there has been a steady increase in the number of process designs and different applications for NPs made via these techniques. With such processes, the number of process variables that can be independently varied is considerable (T, P, flow rate,composition, turbulence of mixing, etc.); thus, these processes offer an almost unlimited toolkit for materials scientists to be able todesign or tailor NPs for specific requirements. For example, a single continuous hydrothermal process could be used to carry out more than one function, (1) control nucleation to make narrow size particles of a specific crystal structure (in a first mixer), and (2) add a surfactant coat that can then be applied inflow (via a second mixer) so nanoparticles can be dispersible inorganic solvents or water (depending on the surfactant). The combination of hydrothermal and microwave/sonochemical synthesis techniques may be a promising approach to significantly reduce the temperature, time, and costs in chemical synthesis. This is interesting not only from industrial aspects but also from a scientific point of view. The reduced heat exposure during synthesis leads to nanosized resultant powder products, where the sizes and shapes of the particles may cover a wide range. This fosters the study of novel nanosized materials with potential for device application.

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Gel-Combustion synthesis

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Abstract

Gel combustion technique is a highly effective method for synthesizing quality material in shorter duration and at lower temperature. This method has been considered as an advanced synthesis procedure that can be utilized for rapid synthesis of many stable and metastable materials. The elementary concept of this synthesis technique will be discussed with respect to application of materials.

Introduction

Major advancement in the field of material science has been observed in last few decades. Industries demand material in various forms like sintered, highly porous, specific microstructure, specific size, stable, metastable, *etc*. Materials synthesis and processing methods have evolved exponentially to furnish the demand of the new improving technologies. Amongst the various synthesis methods, Gel-combustion protocol has been considered to be simple, economic, fast, reproducible, scalable and competent process for the synthesis of materials with distinctive properties.

Gel-combustion is basically an exothermic reduction-oxidation process that occurs among the oxidants and fuel. Oxidants are usually the metal nitrates/oxynitrates; which supply the required oxygen for the combustion reaction. Fuels are organic moiety capable of complexing the ions and getting combusted with an oxidant at low ignition temperature. The compositional homogeneity throughout the constituents should be maintained by the fuel. The powder properties like crystallite size, surface area etc. can be tailored by changing the fuel and also its oxidant-to-fuel ratio. To get the maximum benefit of heat of combustion (ΔH) and to complete the combustion process in one step, the quantity of fuel is determined by the principle of propellant chemistry. The combustion process comprises of two steps,

(i)   Preparation of fuel-oxidant precursor or gel-formation

This stage includes dissolution of the corresponding nitrate/oxynitrate/acetate salts of the metals (in stoichiometric molar ratio) in an aqueous media or dilute nitric acid to obtain a clear solution. An appropriate fuel is added as per the calculated amount to this mixed metal-nitrate clear solution. On thermal dehydration of this solution on a hot plate (at about 80-120 °C) a viscous transparent semi-solid (gel) is obtained. In order to get phase purity and powder quality, any precipitation in the solution, the nature of the fuel, amount of fuel and pH of the solution are also optimized to get clear transparent gel-precursor.

(ii)   Gel-combustion (auto-ignition of the precursor gel to give the product).

The gel-precursor obtained is then heated at elevated temperature to initiate the combustion of the gel. The combustion is either a self-propagating combustion or volume/bulk combustion. The exothermic decomposition of the gel is observed in the form of fire, that swiftly propagates and covers the entire gel in a single step. This step does not require extra external heating and hence termed as "auto-ignition". In case of volume / bulk combustion the continuous combustion happens with large evolution of gases but continuous heating is to be supplied. In small duration of combustion, the product formation takes place in the form a large voluminous powder as a combustion product.

The resultant combustion product obtained could be the required phase, or partially decomposed precursor with carbonaceous residue. Thus this powder has to be subjected to calcination to remove the impurity and obtain the phase pure product.

Oxidant in the gel-combustion

An oxidant in gel-combustion reaction is defined as a salt of the desired metal of which the compound is to be prepared that provides oxygen for the fuel in the combustion reaction. The desired characteristic of oxidants are they should be soluble in water or dilute nitric acid, should not allow precipitation of other cations, should provide the oxygen for the combustion reaction and should give out gaseous by-products so that at the end of the reaction only the desired product is obtained. Metal nitrates, oxy-nitrates and acetates fulfill all the requirement criteria and hence are selected as oxidants.

Fuel in the gel-combustion

A fuel in a gel-combustion reaction is defined as an organic substance/moiety that binds with oxidant and forms a complex with low ignition temperature. It is consumed in a reaction to produce energy and gaseous products. The primary and most important properties of the fuel in the gel-combustion process is capability of maintaining the homogeneity among all the components and must have combustion with the all the reactants (oxidants) simultaneously at a lower ignition temperature.

The desired characteristics of fuel

1. It should sustain compositional homogeneity among constituents.
2. It should form a clear transparent gel and undergo proper combustion with its constituents.
3. It should have low ignition temperature.
4. It should be non-hygroscopic, economic and readily available.

A large variety of organic materials and some inorganic molecules qualify as a fuel for the combustion reaction. However, choice of fuel should be done on the basis of cation used and desired powder properties of the product. Some examples of fuels are e.g. citric acid, ascorbic acid, glycine, urea, hydrazine, hexamethylene tetramine (HMTA), other-α-amino acids, dimethyl urea, EDTA, *etc*. Glycine is considered as one of the best, most commonly used and cheap α-amino acids for gel-combustion reaction. Glycine has a carboxylic acid (-COOH) group at one end and an amino (-NH$_2$) group at the other end that imparts a zwitter ionic character to it which is effectively utilized to bind the metal ions of varying ionic potentials to form complexes and thereby preventing the selective precipitation.

Selection of fuel

Selection of fuel is a very important step in a combustion reaction. As fuel forms complex with oxidant and finally forms a gel, quality of final product, to some extent, depend on this step. The stability of the complexes, the nature of the gel formed, pH of the precursor gel, the auto-ignition temperature, all depend upon the selection of proper fuel. The formation of desired phase, powder properties of the material thus depend lot on the fuel selection. The selection of fuel should be based on stability of the gel obtained for auto-ignition and Thermodynamic and thermal stability of the product

Amount of fuel

Amount of fuel plays a very important role in gel-combustion method. As per the rule of propellant chemistry ,to get a stoichiometric redox reaction between a fuel and an oxidant, the ratio (ϕ) of net oxidizing valency of oxidants to net reducing valency of fuel (O/F) should be one. An example of calculation of these valencies is elucidated below.

For synthesis of nanocrystalline Gd$_2$O$_3$.

The oxidizing valencies calculated for the oxidant viz., Gd(NO$_3$)$_3$·6H$_2$O is 15-.The reducing valency of the fuel viz., glycine is 9+. The oxidizing and the reducing valencies are calculated as follows:

(i) Gd(NO$_3$)$_3$·6H$_2$O: (Oxidizing valency of Gd = 3+, N = 0) (Reducing valency of O = 2-)
    Thus the net oxidizing valency = 15-
(ii) NH$_2$CH$_2$COOH: (Oxidizing valency of N = 0, H = 1+, C = 4+)
    Thus the net reducing valency = 9+

The valencies of C and N are taken as 4+ and 0, as these species are lost as CO_2 and N_2, respectively, during the combustion process. The ratio of O/F valency then turns out to be 1:1.66 is called as (Φ), this is the stoichiometric ratio. The O/F ratio lesser than 1.66 is termed as the fuel-deficient ratio and O/F ratio greater than 1.66 is called as fuel-excess ratio. This O/F ratio is an important factor as it governs the flame temperature and heat of the combustion process.

Selection of fuel to oxidant ratio

Combustion can be performed in various oxidant-to-fuel ratio, *i.e.*, from fuel-deficient ratio to fuel-excess ratio. The nature of combustion and obtained powder would vary in properties for different oxidant to fuel ratio.

Precautions

The auto-ignition process of gel-combustion is prompt and vigorous with a large amount of heat and gas release for very short duration. Combustion process is known for its simplicity but, a few precautionary measures are necessary:

(i)   Proper information about the fuel and its behavior should be compiled. Initially small batch reactions are useful to understand the behavior of the fuel and the oxidants.
(ii).   The combustion experiments should be carried out in fume hood. For a large batch of combustion, an arrangement for proper and safe ventilation should be done.
(iii)   Combustion process should be carried out in a wide mouthed apparatus, with large volumes to avoid any pressure build up.
(iv).   Combustion-synthesized powders are highly reactive as their surface area is large and surface energy is high. Proper conditions of calcinations and storage is required to avoid any deterioration in powder properties.

Thus it can be said that with proper knowledge of reactants, combustion process and safety guidelines, combustion reaction can be easily carried out to synthesize innumerable products that can be used for various applications.

Conclusion

Combustion technique has the capability of delivering ultra-fine nano-powders in shorter duration of time with a lower calcination temperature. The material obtained via this method offer tunable powder properties which allow application in various fields. One of the important aspects regarding the combustion process is the tailorability of the processing conditions to obtain metastable phases. With varieties of modification applied in this process, this technique has opened up a new direction of synthesis protocol to design the material for technological demands.

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Synthesis of materials under high pressure/ high temperature conditions

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Abstract

Preparative chemistry under high pressure is an interesting and challenging process evolved with the progress of materials development. The application pressure in synthesis often provides an alternate pathway to obtain desired materials and also to overcome the conventional crystallographic and thermodynamics constraints. Thus, the synthesis under high pressure and temperature can lead to materials which otherwise would not be possible to prepare by normal high temperature processes. Materials with unusual coordination number, valence states, packing density can be prepared by application pressure to a normal high temperature synthesis procedure. This process also enables to prepare mineralogical and planetary materials in the laboratory. In this presentation, a brief overview on the reaction at high pressure and effect of pressure and pressure/temperature on the chemical reaction will be presented. Typical examples of materials synthesized under high pressure conditions will be discussed.

In general synthesis of material is a process of transformation of some material(s), called reactant(s)/precursor(s), to another material called product by using some perturbation in temperature, pressure, environmental composition. These perturbations are mainly aimed to overcome the activation energy, i.e., the energy barrier for the transformation from reactant to product. In all chemical reactions, the chemical equilibrium and free energy of reactants and products are essentially considered for designing an appropriate synthesis procedure. The understanding of the effect of pressure, temperature and compositions on chemical equilibriums provides information for the suitable or mostly desired thermodynamics parameters for designing a synthesis procedure. Besides, the synthesis under more than one thermodynamic variable follows alternate mechanism to the formation of product. This has been adopted in nature in the formation minerals and materials in the interior of earth. The use of pressure for chemical and physical processes knowingly or unknowingly has been exploited by the mankind since long. However, the effective use of pressure and requirement of high or low pressure came to picture of materials synthesis after the development and understanding of thermodynamics and kinetic of chemical reactions. Thus, for a given reaction scheme, temperature and pressure are considered as the most important thermodynamic parameters for synthetic chemists, where the chemical equilibrium and hence the direction of chemical reaction can be controlled.

In general, any material gets destabilized by application of pressure or temperature or both. This can be attributed to the deviation of interatomic distances from their equilibrium values and that leads to increase in the free energy, and by convention any system tends to get stabilized by lowering its free energy. The destabilized state of material tends to decompose, reacts with surrounding materials to form a different product, transforms to stable structure/phase, or remains as a metastable phase with higher energy than obviously expected. Besides these phenomena, there can be several changes in non-structural parameters, like pores and grain growth happening due to the simultaneous application of pressure and temperature. Also, pressure can bring grains of the reactants to maximum possible proximity, and hence diffusion of ions among the reactants becomes easier. Thus, controlling or facilitating the diffusion process by application of pressure and temperature favour for grain growth and hence sintering. Thus, simultaneous application of pressure and temperature is extensively used to prepare sintered ceramics.

In general, in a solid-state reaction, two or more solids reacts with each other to form a single solid again, and hence no change in entropy of the system occur. Obviously, pressure and temperature both increase internal energy of the system, and hence the decreases in free energy relies

predominantly on the decrease in volume. Thus, often the pressure assisted syntheses are driven by decrease in volume, and hence denser or compounds with lower molar volume are preferentially formed. Thus, the syntheses under high pressure and the phases formed under high pressure are the cumulative effects of several factors and some of the important factors are as below.

- Bond lengths shortened and interatomic repulsion becomes dominant.
- Force constant increases, rigid polyhedra are formed.
- Coordination number increases and introduces newer interaction between atoms or ions.
- Tends to form closely packed structure.
- Leads to denser structure by reduction of empty/free volume in the structure.
- Alters the electronic configuration, like delocalization of charges, separation of charges, and alteration of electronic arrangement in orbitals.
- Decreases in vibration parameters (U).

The synthesis process and equipment of synthesis vary depending on the requirements of the reaction and that can be provided by compressed gassed or liquid or by direct compression of solids. However, high-pressure synthesis carried out by liquid as well as gas pressure usually remains to limited pressure. This is mainly arising from the container materials. The synthesis carried out by the autogenous liquid pressure is categorised as solvothermal or hydrothermal and they themselves form class of state of art synthesis method. Similarly, the pressurized gas method is also limited to low or moderate pressure and often the gas is selected as one of the reactants. This helps to attain materials with unusual oxidation state, novel or off stoichiometric compositions. Most commonly the solid-state reactions at moderates to high pressure are carried out by physical (mechanical) compression of reactants in between two plates, called anvils, moving towards each other. The anvils, are a pair of moveable heads made from super hard materials like hardened steel, WC, diamond, etc. As, the pressure is defined as force per unit area, the increasing force on the anvils or decreasing cross-sectional area of the anvils increases the pressure. In general, the sample is placed in a confined space and compressed mechanically by applying force on anvils. The experimental setups are designed accordingly to drive force at the sample under study. Usually decreasing area, is a convenient mode to enhance pressure to very high values, and there the use and evolution of diamond anvils arise. Hence, synthesis or study of materials at extremely high pressure relies on the diamond anvil cell. But the sample volume is limited due to extremely small volume of the compressed region. Synthesis of large volume materials most commonly carried out by piston cylinder apparatus, Bridgman anvil, Toroid anvil, and belt apparatus, multi-anvil setup. In all these setups, the common instrumental features are anvil, pressure chamber, spacer or gaskets and pressurizing or pressure transmitting medium, while the design of anvils makes them different. The anvils approach each other and squeeze the pressure transmitting medium in between them. The gaskets hold the pressure transmitting mediums as well as prevent the anvils to touch each other and house the sample under study. In high pressure and high temperature synthesis, the temperature generation is second challenging part of the experimental setup, and only limited options are available due to complicated mechanical arrangements of anvils. The sample holder is heated in most of the high-pressure setup, while the pressure cell is heated in some cases. In both cases, the limitation arises from the construction materials and their thermal conductivity and thermal stability. Usually, graphite, $LaCrO_3$, SiC and $MoSi_2$ like resistive heating elements are used as collar to the samples and placed inside the pressure chamber, and as high as 2000°C under pressure can be generated by such heaters. At very high pressure, as in diamond anvils, high temperature is generated by heating the sample by laser beam. High temperature around 5000°C in the diamond anvil can be generated by such laser heating.

Crucial role of pressure in synthesis of materials have been demonstrated in a variety of materials, and often to prepare unknown and metastable materials. As mentioned earlier, the materials prepared under high pressure and temperature are unusual in the sense of their structural and thermodynamical properties. Some of the examples are briefed here. The ABX_4 type compounds are known to exist in diversified structures depending on the nature and ionic radii of and B cation and X anions. A case like single phase $LiScF_4$ does not form in a ambient pressure solid state reaction of LiF and ScF_3. Due to smaller ionic radius, Sc^{3+} prefer octahedral coordination with fluoride ions, and that

preferentially leads to the formation a mixture of Li_3ScF_6 and unreacted ScF_3. However, under high pressure and temperature conditions $LiScF_4$ form a scheelite type structure with ScF_8bisdisphenoid and LiF_4tetrahedra. Similarly, orthorhombic $InVO_4$ and triclinic $FeVO_4$are formed easily under ambient pressure high temperature reaction of Fe_2O_3/In_2O_3 and V_2O_5. Both the compounds are formed with usual tetrahedral VO_4 units. However, synthesis under high pressure and high temperature, or application of pressure on orthorhombic $InVO_4$ or triclinic $FeVO_4$ transform to rutile or related structure with octahedral VO_6 units. By application pressure, the ions come closer to each other, and that rearrange position of atoms and transforms the low coordinated polyhedra to high coordinated polyhedra. The transformations in these cases are irreversible and hence the high coordinated and denser phases can be retrieved by releasing the pressure. However, these metastable phases can be transformed to their corresponding stable phase by application of temperature. Another case, is that scheelite type rare-earth vanadates with smaller rare-earth ions can be prepared by applying pressure on their stable zircon type phases. The increase in packing density by application pressure transforms the zircon type phases to the scheelite type phases. A denser phase of $HfMo_2O_8$ or $ZrMo_2O_8$ has been prepared by application of pressure and moderate temperature to trigonal $HfMo_2O_8$ and $ZrMo_2O_8$. The increasing coordination number of Zr^{4+} or Hf^{4+} from size to eight increase the packing and form these metastable phases. Though only few cases of high-pressure synthesis are mentioned, a large number of examples, like synthesis of noble gas compounds, perovskites and pyrochlores with ions of uncommon radius, materials with ions of unusually high oxidation state, Complex compositions, synthetic minerals, *etc*. are reported in literatures.

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Chemistry at Engineering Scale

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Chemical engineering is all about the conversion of raw materials into beneficial products. Typically, a batch, semi-batch or continuous process is used for chemical production. Reactions or separation processes involved in conversion of raw materials or reactants to beneficial products are developed in laboratory at very small scale. This requires performing large numbers of experiments to quantify the reaction kinetics, thermodynamic values, physical, thermo-physical and transport properties data associated with reaction or separation. More often than not, the process output depends on multiple parameters. Identification of the optimum values of these parameters to maximize the desired objective (e.g. reaction yield, purity of the desired product) is best done in lab-scale, as it may require a large number of experiments conducting which at larger scale may not be practically possible and economically feasible. At lab-scale chemistry (kinetics, thermodynamics) is the most important aspects. However, to realize the reasonable production rates, scale-up to engineering scale is necessary. Laboratory scale data is indispensable to design the engineering scale equipment. For example, an engineering scale reactor cannot be designed if the reaction kinetics, which is typically obtained in lab-scale experiments, is not available. Similarly, an engineering scale distillation column cannot be designed if the vapour-liquid equilibrium data, which is typically generated in lab-scale experiments, is not available. While availability of the lab-scale data is a necessary condition to design engineering scale systems, it is not a sufficient condition. At engineering scale, as the dimensions of the equipment increase, non-ideal flow becomes an issue which, if not accounted in the design, may be detrimental to the performance of the equipment. For example, while a magnetic stirrer is good enough for mixing at lab-scale, a proper design of impeller is needed for an engineering scale stirred tank to avoid flow non-idealities such as dead zones and bypassing. Similarly, issues such as heat integration, minimizing inventory, reduction in plant foot print, safety and environmental impact become important at engineering scale.

Development of chemical and nuclear chemical processes is a key activity at Chemical Engineering Division (ChED), BARC. This typically involves conducting lab-scale experiments to assess feasibility, generating the data required for design and scale-up to engineering scale (bench-scale/ pilot-scale/ plant-scale). Lab-scale data are also used for validation of mathematical and computational models which, after validation with lab-scale data, can be used for design and scale-up studies. This abstract provides some examples of process development activities at ChED highlighting transition from lab-scale experiments to engineering scale systems.

Development of fluidized bed thermal/thermo-chemical denitration processes to treat nitrate bearing streams (such as ammonium nitrate) which are generated in different processes in nuclear fuel cycle, is a key activity at ChED. The decomposition reaction of ammonium nitrate at typical operating temperatures ($\sim$385 ^{0}C) is given by Eq. (1).

$$2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O \quad (\Delta H = \text{-118.86 kJ/mol, T = 385 }^0\text{C}) \quad (1)$$

Initially, the process feasibility of thermal denitration of ammonium nitrate was tested in 3" diameter lab-scale fluidized bed reactor, shown in Fig. 1. Subsequently, the process was demonstrated in 6" diameter bench-scale as well as 12" diameter pilot-scale reactors. In lab-scale and bench-scale reactors, the process parameters - operating velocity ratio (u/u_{mf}), aspect ratio (h/D), nozzle air to liquid ratio (ALR), and bed temperature were optimized for maximum decomposition of ammonium nitrate. In pilot-scale, the reactor throughput was increased adopting multi-nozzle feed injection to match with industrial

requirement. The technology has been deployed in the back-end of the nuclear fuel cycle. From the scale-up experience, the aspect ratio of the plant-scale reactors was kept higher which has yielded a higher conversion of ammonium nitrate (~ 80%).
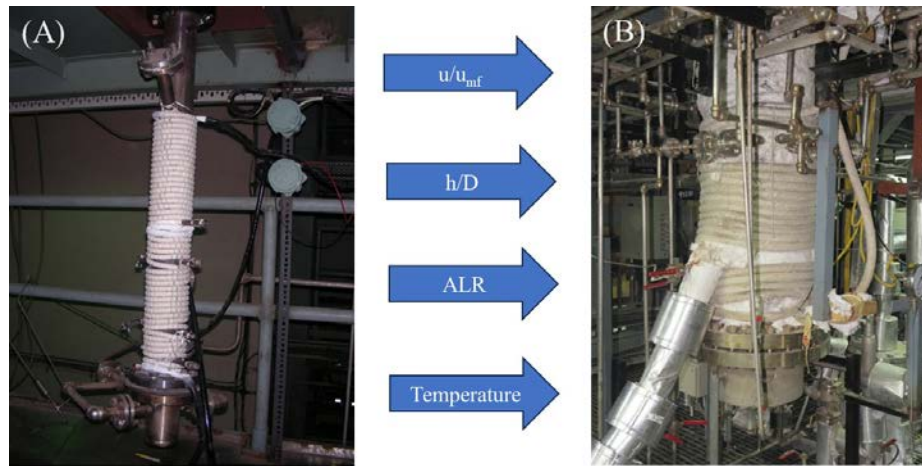
Figure 1: (A) 3" diameter resistance heated lab-scale fluidized bed reactor (B) 18" diameter induction heated engineering-scale fluidized bed reactor deployed in spent nuclear fuel reprocessing facility
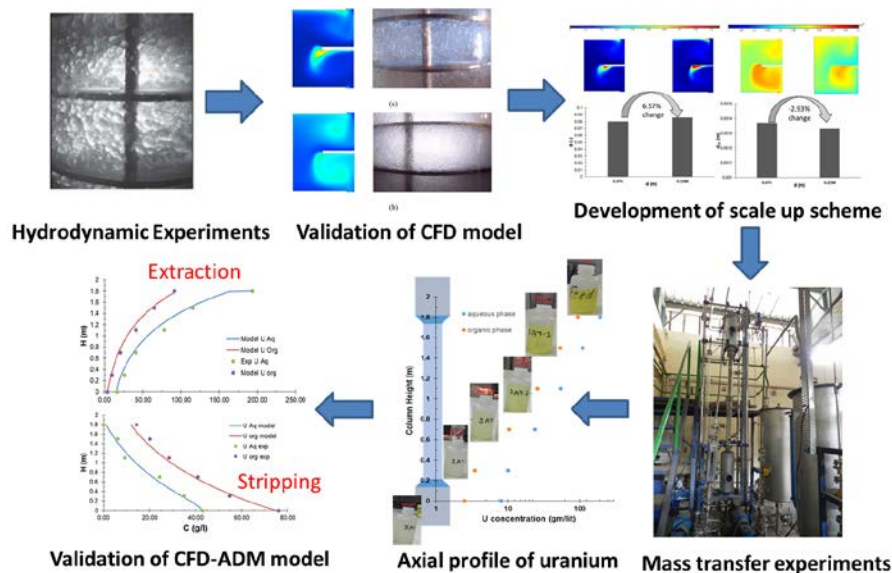
Figure 2: Work flow for utilizing lab-scale data to design engineering scale PDDC for uranium refining in the front-end

The next example of transition from lab-scale to engineering scale is Pulsed Disc and Doughnut Column (PDDC), a solvent extraction equipment being developed for intensification of uranium refining process in the front-end. The development work involves carrying out lab experiments to determine the liquid-liquid equilibrium using the feed (crude uranyl nitrate solution) and the solvent (30% tributyl phosphate in dodecane), studying hydrodynamics (drop size, dispersed phase holdup and axial dispersion, flooding throughput) in pulsatile liquid-liquid two-phase flow in lab-scale PDDC (2-3 inch diameter, 0.5 m length), developing Computational Fluid Dynamics (CFD) models to predict hydrodynamics and their validation using the lab-scale column data, and utilizing the validated models for scale-up. The liquid-liquid equilibrium data generated in lab and CFD models validated with lab-scale column data have been

utilized to design the engineering scale column (3 inch diameter, 1.5 m height) which has been successfully tested for uranium extraction. The work flow of this activity is shown in Fig. 2. The data from engineering scale PDDC are being used for further scale-up.

ChED is also carrying out process development of copper-chlorine thermo-chemical cycle of hydrogen production, which is one of the most prospective processes for generation of nuclear hydrogen. This thermo-chemical cycle involves four steps through which the overall chemical reaction of water splitting is realized to produce hydrogen with oxygen as the byproduct. Two of the four steps are hydrolysis and thermolysis which owing to being high temperature steps are known as thermal steps. Scale-up of these thermal steps has been carried out from lab-scale to engineering scale. Hydrolysis reaction, given by Eq. (2), is carried out in fluidized bed reactors shown in Fig. 3. Reaction is an endothermic reversible gas–solid reaction. Experiments and modelling done at lab-scale (reaction kinetics, optimum reaction temperature and steam to Cu ratio for maximizing conversion, understanding of transport phenomena, model of the reactor validated with lab-scale data) have been utilized to design engineering scale reactor, as shown in Fig 3. Design of engineering scale reactor also involves designing auxiliary steps for seamless integration of the hydrolysis step with other steps of the process.

$$2\ CuCl_2\ (s) + H_2O\ (g) \leftrightarrow Cu_2OCl_2\ (s) + 2\ HCl\ (g)\quad (\Delta H = 113\ kJ/mol,\ T = 325\ ^0C)\quad (2)$$
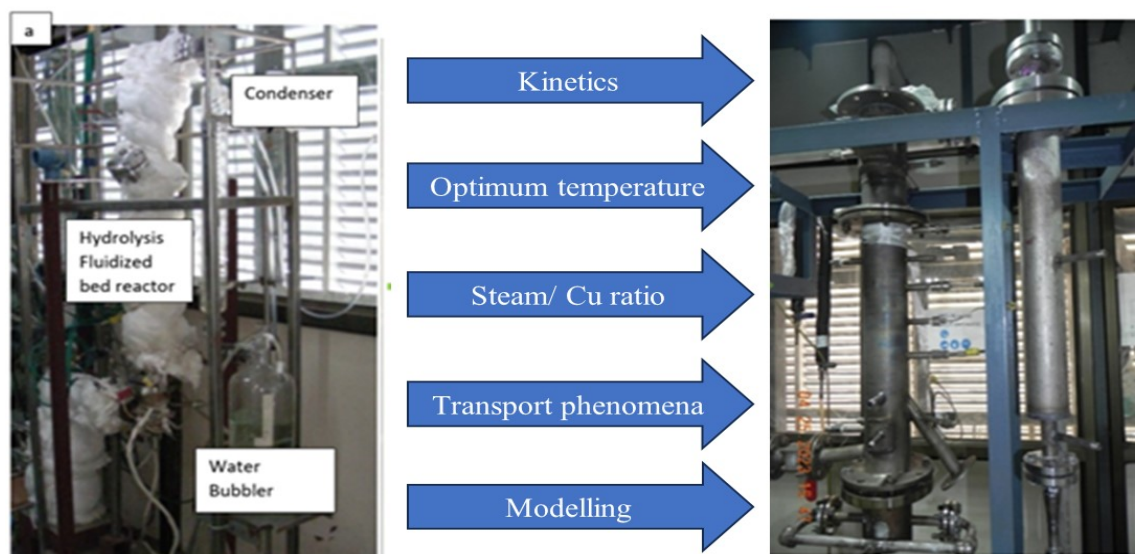
Figure 3: Lab-scale 2" diameter hydrolysis reactor (left) and engineering scale 4" diameter hydrolysis reactor

Hydrolysis is followed by thermolysis reaction, which is given by Eq. (3).

$$Cu_2OCl_2\ (s) \rightarrow 2CuCl\ (s) + 0.5O_2\ (g)\quad (\Delta H = 113\ kJ/mol,\ T = 325\ ^0C)\quad (3)$$
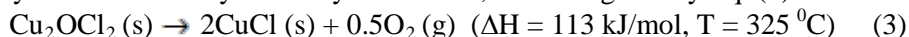
Thermolysis reactor is a slurry bubble reactor. It has also been scaled-up from lab-scale to engineering scale. Identification of elementary steps of the reactions, kinetics of solid state chemical reaction, development and validation of the model of the reactor coupling reaction and heat transfer have been done in lab-scale thermolysis reactor. The lab-scale data and models have been utilized for designing engineering scale thermolysis reactor.

Another example of scale-up at engineering scale is synthesis of di-tertiary-butyl-di-benzo-18-crown-6 (DTBDB18C6). DTBDB18C6 is precursor to di-tertiary-butyl-di-cyclo-hexano-18-crown-6

(DTBDCH18C6), which is used for extraction of strontium from high level liquid waste generated from spent nuclear fuel reprocessing. Reaction for synthesis of DTBDB18C6 is given by Eq. (4).

$$(4)$$
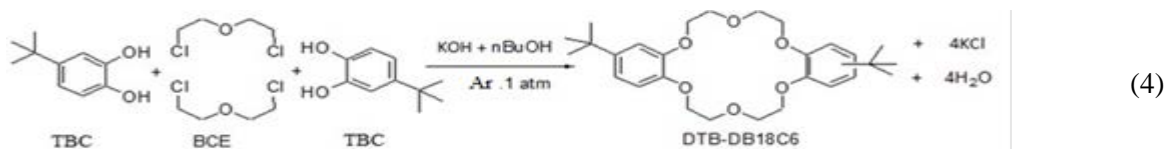
Initially, the process feasibility of synthesis of DTBDB18C6 was tested in small size glass reactor. Subsequently, the process was demonstrated in 85 litre hastelloy pilot-scale reactor. In lab-scale and engineering scale reactors, the process parameters – contact time, reaction temperature, sequence of addition of reactant and rate of addition of reactant were optimized for maximum conversion of reactant and yield of product DTBDB18C6. Scale-up of reactor from lab-scale to engineering scale is shown in Fig 4. At engineering scale, the reactor throughput was increased by increasing volume of reactor at optimized parametric condition.
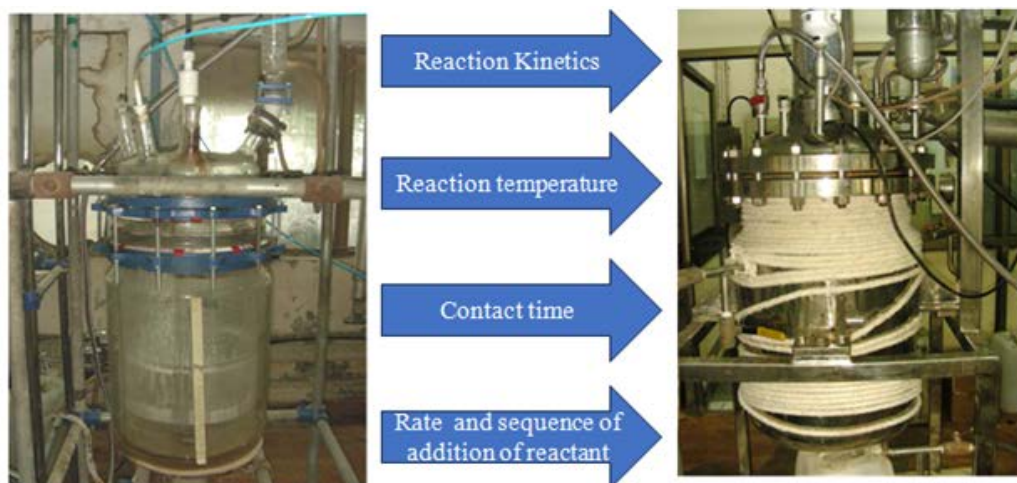
Figure 4: Lab-scale glass reactor (left) and engineering scale 85 L hastelloy reactor for synthesis of DTBDB18C6

Ionic liquids, which are considered as the green solvents, have several potential applications. ChED has developed the technology for synthesizing imidazolium-based ionic liquids such as (1-butyl-3-methylimidazolium bromide) at kg/day scale using microreactor technology. Such reactions, for example, synthesis of 1-butyl-3-methylimidazolium bromide from 1-methyl imidazole and 1-bromo butane, given in Eq. (5), is highly exothermic. This makes use of microreactors, which provide high surface to volume ratio for very efficient heat management, very attractive for carrying out such reactions. The development of technology involved carrying out synthesis in very small microreactors at gm/day scale. The experiments done at small microreactors helped identify the optimum residence time required for almost complete conversion, maximum reaction temperature which can be used without thermal degradation of the product to maximize space-time yield and quantification of pressure drop. These data have been utilized in engineering scale microreactor system which can give production rate of the order of kg/day. The lab-scale and engineering-scale setups are shown in Fig 5.

$$(\Delta H = -96 \text{ kJ/mol}) \quad (5)$$
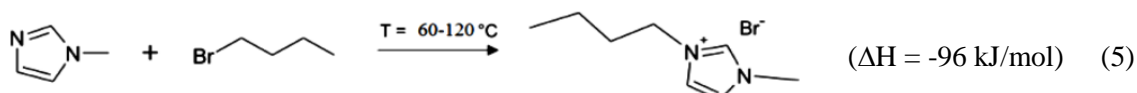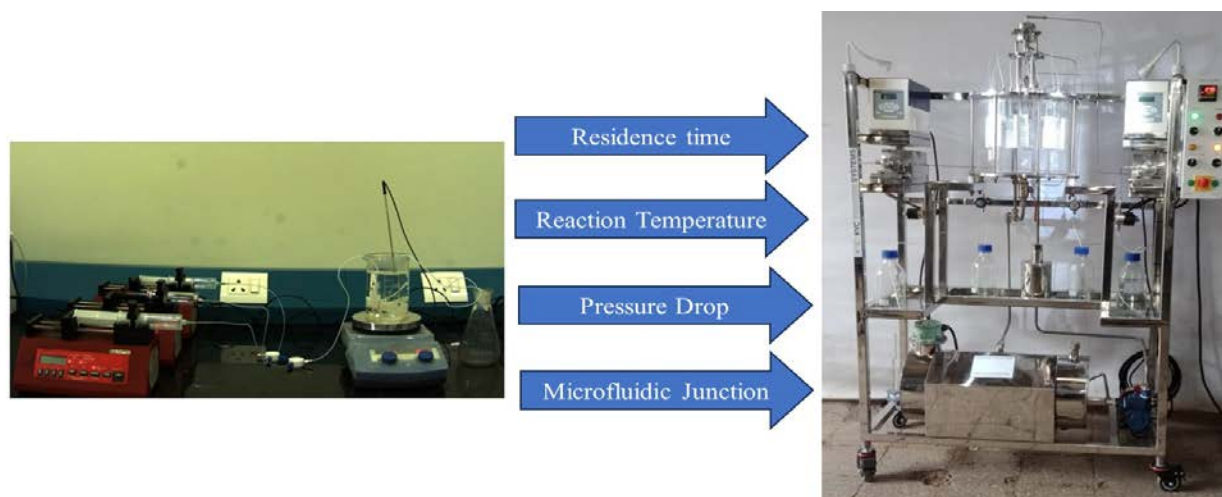
Figure 5: Lab-scale microreactor setup (gm/day scale) and engineering scale (kg/day) microreactor setup

The above mentioned cases represent the role of scientific parameters which are relevant for effective application of chemistry established in small scale to a technology in engineering scale. Computational modelling plays a crucial role in minimizing number of experiments and prediction of results, where real experiments cannot be performed. However, data generated through practical experiments are still considered as most reliable till date.

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Sintering of ceramics

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Abstract

Inorganic compounds (oxides, borides, carbides and nitrides) having high melting temperature and inherent brittleness are called Ceramic materials. Different ceramic components are prepared by sintering a green compact prepared though different shape forming methods. The process of densification of a green compact by firing at high temperatures, leading to bonding among the particles is called sintering. This sintering process proceed through stages. Decrease in surface free energy is the driving force for the process. Mass transfer takes place due to chemical potential difference between two points. There are different pathways through which mass transfer takes place. Sintering techniques are generally classified based on diffusion pathway and type of applied field / heating to assist in sintering.

Sintering phenomenon

Sintering is a process in which a green compact is heat treated at high temperatures to give a dense structure as a result of strong bonding between the particles[1]. Coherent bonding between the particles leads to decrease in porosity in the green compact. These strongly bonded structures generate different microstructure. Some of the properties that depend on microstructure are mechanical strength, dielectric strength, electrical conductivity, etc.,which improves upon sintering. Compaction in green state offers handling strength and deprive of required functional properties, which depends on density. Hence, sintering not only gives strength but influences some of the microstructural and density dependant properties.

Driving force for sintering

The driving force for sintering process is the decrease in surface free energy of the system. There is a large change in the surface area of the particles, which leads to decrease in surface free energy of the system. Mass transfer is the basis to fill the pores and the particles loose its identity. Chemical potential at a point depends on surface free energy and chemical composition. Mass transfer takes place due to chemical potential difference between two points.[2]. The various mass transport phenomena are surface diffusion, viscous flow, plastic flow, vapour transport, volume diffusion, and grain boundary diffusion [3]. Fig.1 depicts different mass transport phenomena during sintering process.
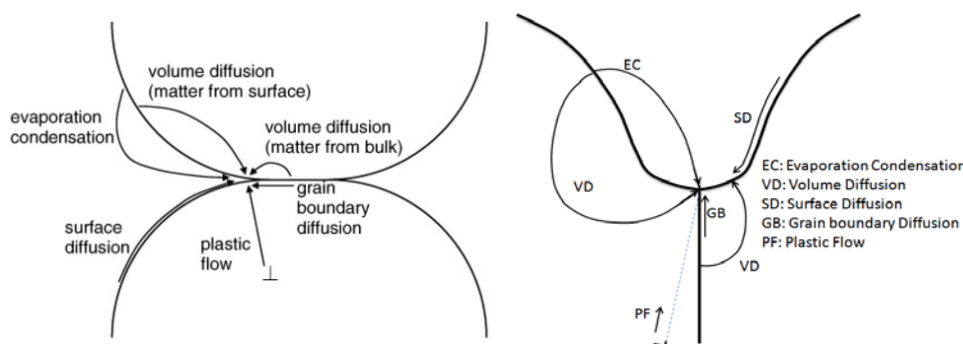

Figure 1. Mass Transport processes at the contact point between three particles

Stages of Sintering

When a green compact is heated at high temperatures, there is a change in porosity and microstructure. Stages of sintering defines this progressive changes in microstructure with temperature. In the first stage of sintering where neck formation between the particles takes place and neck growth with other contacting particles are independent of each other. Initial step is limited to neck growth up to 0.4-0.5 of the particle radius. Growth at neck region is associated with material deposit at the neck. In this process, gradient in the curvature decreases and surface becomes smoother. Initial stage is limited to neck formation and a small neck growth. In the intermediate stage the major change includes, densification, rounding of pores and grain growth**[4]**. As curvatures are smoothened in the beginning of the second stage the surface energy change is the driving force in this stage **[5]**. With neck growth, stable pores are generated at the grain edges.These cylindrical pores around the grain edges are continuous and distributed. At the end of the second stage, pore rounding takes place and pores are isolated at the grain corners. Both co-ordination number of pores and grains are frozen.

Third stage is quite important in getting full density in the material. In the final stage densification is very slow. Final stage starts when continuous cylindrical pores break into discrete pores. These pores are adherent to the grain corners. Coarsening is a competing phenomenon with densification in this stage. Pores may either attach to the grain boundary or may stay inside the grains. Spherical shape of pores is visualised if the pore is inside the grain. Lenticular pore structure is generated when pores are attached to the grain boundaries.

Factors affecting sintering

Sintering is aimed at getting a dense product of desired shape, size, and density with necessary functional properties. As many factors affect sintering at different stages, their role has to be meticulously monitored. These factors are powder quality (size and distribution, degree of agglomeration), powder packing, additives (composition, impurity, and liquid phase), temperature/heating rate, atmosphere, external field, and applied pressure. Sintering is influenced by the interaction of particles, pores, grain boundaries, impurity, and atmosphere. Experiments are designed at different conditions to observe the contribution of each.

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Chimie-Douce Approaches in the Synthesis of Novel Inorganic Solids

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Abstract

Synthesis plays a key role in realizing new structures and materials properties. It has been realized that the progress in metal oxide based materials chemistry critically depends on the synthesis of new solids with unique structures and properties. While one can imagine a huge number of compounds in the compositional space of inorganic oxides, many are not attainable at all under the experimental conditions insofar endeavored by researchers. Often it is not the case that an imagined composition is not achievable at all, but could not be synthesized by conventional synthesis at elevated temperatures. Although, the conventional solid-state and other syntheses methods employing high temperatures is beneficial and widely employed for the synthesis of many functional oxides, the range of compositions accessible is again limited due to the competition between the thermodynamic and kinetic factors. This often leads to the formation of thermodynamically stable products, leaving many envisioned compositions out of reach due to their metastable nature. In this context, *Chimie-douce* or soft-chemistry based approaches have been very successful for the stabilization of many metastable oxides, which were otherwise inaccessible. Most of the time, if the emergent compound is metastable, it gets arrested in a local minimum of its potential energy landscape and thus is not achievable under harsh reaction conditions involving high temperatures. Thus, soft-chemistry based approaches are of immense interest in the synthesis of novel inorganic solids and proved to be very powerful in the expansion of compositional space by realizing a large number of new and unusual materials. Among the soft-chemistry approaches, ion-exchange, intercalation and metathesis are noteworthy.

Ion-exchange is one among many soft-chemistry techniques that have been exhaustively employed for the synthesis of a large variety of compounds with structures ranging from open-frame work solids, clays, layered double hydroxides and tunnel structured to layered compounds. While topotactic ion-exchange in open-framework solids and oxides with layered and tunnel structures has resulted in the formation of a variety of metastable functional materials, these ion-exchanges are primarily limited to the above structure types due to the presence of labile ions as loosely held charge-compensating cations or anions in open channels/tunnels or the lability of the charged motifs in the interlayer galleries of the layered oxides. For example, topochemical reactions have been widely employed on layered perovskites for the development of a variety of new compounds at low temperatures. Dion−Jacobson (DJ) and Ruddlesden−Popper (RP), are the two prominent structural families of layered (two-dimensional, 2D) oxides found to be highly receptive to ion-exchange of the interlayer alkali cations. The greatest advantage of ion-exchange reactions is that they are cost effective as most of the time the reactions are carried out at room temperature and in aqueous medium. While these topotactic exchanges are quite common in the above mentioned structure types, butare rare in the three-dimensional (3D) close-packed structures based solely on corner- or edge connected polyhedral networks. Recently, there have been reports of ion-exchange in 3D-mixed metal oxides with octahedral connectivity enabling the development of metastable functional oxides with diverse structures and properties. For example, ultraviolet-absorbing diamagnetic insulating oxides can easily be transformed into visible-light-active paramagnetic semiconductors. As examples, ion-exchange in the family of 2D layered perovskites, 3D perovskites, rutile and α-PbO$_2$ structure types will be discussed.

In addition to ion-exchange, intercalation is yet another soft-chemistry based technique wherein ions can be inserted in vacant positions of the crystal structure with ease and under relatively low-temperature conditions. The intercalation reaction has also been proven to be very effective in

realizing some of the interesting oxide chemistry. The reverse of intercalation is deintercalation, that is extracting out the ions from specific sites of a structure. Since the intercalation and deintercalation involves the incorporation and removal of ions to/from a structure, these is a situation of charge imbalance, which give rise to reduction/oxidation of metals present in starting host. This makes the intercalation reaction usually reductive in nature while the deintercalation reactions are oxidative. Reductive intercalation of alkali metals is very common in layered transition metal oxides and sulphides. The intercalation and deintercalation can be carried out both chemically and electrochemically. Practical demonstration of electrochemical intercalation and deintercalation of lithium ion in layered structured oxides/sulphides led to the successful development of Li-ion batteries (LIBs). In addition to electrochemical methods, chemical intercalation of Li/Na have been proven to be of considerable interest as soft-chemical avenues for the synthesis of several metastable materials. Moreover, Li have been oxidatively deintercalated from layered hosts to give rise to the formation of several metastable oxides. The oxidation deintercalation is not only limited to the layered oxides and sulphides, it has been extended to the framework phosphatesas well. Series of intercalation and deintercalation reactions have also been carried out to demonstrate construction of new structural layers within an existing structure. Prototypical examples from layered oxides, sulphides and NASICON based framework phosphates undergoing intercalation and deintercalation reactions will be discussed.

Apart from the ion-exchange and intercalation, solid-state metathesis (SSM) offers another not-so-soft route that uses moderate temperature conditions for the synthesis of thermodynamically stable as well as metastable solids. The solid-state metathesis is also known as double decomposition reaction, where the desired product phase is accompanied by one or two byproduct(s) which can be separated from the mixture by simple washing. The reactions are so designed that the byproducts are either gaseous substances (which can easily escape) or ionic solids (mostly soluble in water). The driving force or spontaneity of these reactions originate from a large negative enthalpy change in the reactions due to the formation of ionic salts releasing large amounts of lattice energy. The reactions are generally highly exothermic and self-propagating thus often less energy demanding and requires shorter durations. The solid-state metathesis also allows for microstructural modifications in the resulting materials. Examples of typical SSM reactions from the literature will be discussed.

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Flow Control Refractories for Steel Casting: Role of Materials Chemistry

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India is one of the biggest producers of TMT bars, known as construction steel, worldwide. Materials chemistry plays a significant role in producing the right quality flow control refractories, for continuous casting of steels. The current talk will describe the manufacturing processes for shaping the ladle and tundish refractories. The materials include alumina-carbon, alumina castable and Mg-stabilized zirconia, whereas shaping methods include pressing and sintering as well as vibro-casting. The science and technology of manufacturing advanced Mg-stabilized zirconia refractory/technical ceramic components will be discussed in detail.

Dr. R. D. Purohit joined Powder Metallurgy Division of BARC in 1994 through 37th Batch of Training School after completing his master from Jodhpur University. He did his Ph.D from Mumbai University followed by Post-Doctorate from Jean Rouxel Institute of Materials, France. His R&D pursuits involved development of technical ceramics for nuclear and societal applications. He has extensively worked on innovative synthesis methods of ultrafine oxide ceramic powders and their sintering behavior. He has published 28 research papers in journals of international reputation including Journal of American Ceramic Society, American Chemical Society, Royal Society of Chemistry, Material Research Bulletin, Journal of Nuclear Materials and Encyclopedia of Nano-Science and Nano-Technology. In 2019, he took voluntary retirement from BARC to scale up and commercialize his professional experience to serve refractory and steel plants industries by setting up the company "Zirconia Refratech Pvt Ltd." He is currently working as Director-Technical and Managing Director of this company. He is also a partner in company called "Advanced Technology Materials" which deals in Rare Earth Chemicals, Refractory Metals and Technical Ceramic Powders and Components.

Soft matter assisted synthesis of advanced healthcare materials

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Taking cue from the principles of soft matter is a fruitful approach in the design of several technologically relevant advanced materials. One essential feature in soft matter is that they are composed of mesoscopic entities held together by interaction energies comparable to thermal energy. Colloids, polymers, liquid crystals, surfactants etc. are typical examples that form soft materials under appropriate conditions. As the name implies they can be easily deformed by external forces and have shear modulus three to six orders of magnitude smaller than atomic solids. High molecular weight polymers such as polyacrylic acid or gelatin, a biopolymer derived from collagen, in aqueous medium forms a gel with a high volume fraction of water which are classic examples of soft materials. Amphiphilic molecules or surfactants can self-assemble in selective solvents to form a variety of structures such as micelles, vesicles and lyotropic liquid crystals. Such self-assembled structures can act as the structural unit to form soft matter under appropriate conditions. Cooperative assembly of organic surfactants and inorganic precursors can be employed for the successful creation of inorganic/organic mesostructured composites with tailored functionalities. This lecture will address some of the guiding principles in the design and synthesis of advanced materials using soft matter systems with special emphasis on healthcare materials.

Introduction to soft matter

Soft matter is ubiquitous in nature. It exploits self assembly to create many intriguing structures with diverse morphologies and mechanical properties. The macroscopic properties of materials are largely dependent on the strength and length scale of intermolecular interactions between the moieties that constitute the matter. The principal quantity that tells how "hard" or "soft" a material is its shear modulus. Rheological measurements provide information about this property and it depends on the time scale at which it is probed. In general, the two limiting cases of rheological properties of a liquid and a solid can be generalized in terms of flow and elasticity respectively. Flow is an irreversible deformation which is the characteristic of a liquid while elasticity is a reversible deformation characteristic of a solid. Many soft matter systems exhibit both viscous and elastic properties. Thermal fluctuations play a dominant role in such systems due to the presence of weak non-covalent interactions exists among them. This enables the system to reach thermodynamic equilibrium state and also transform among different structures under the influence of an external stimuli.

Design of molecular self-assembly

The occurrence of equilibrium structures of amphiphiles with finite aggregation number and its dependence on molecular structure has been envisaged in the primary work of Tanford and later extended by Israelachivli and others. Optimal packing of molecules in the aggregate, based on geometrical constraints, led to the development of a predictive geometrical parameter known as critical packing parameter (CPP) which is used as a guiding principle to forecast the geometry of aggregates. The packing parameter of an amphiphile can be defined by

$$CPP = \frac{v}{a_0 l}$$

where, v is the volume of the hydrophobic part, l is the length of the hydrophobic chain and the a_0 is the effective head group area of the surfactant molecule.

Figure 1. Schematic illustration of microstructural changes in assemblies formed by amphiphiles by changes in the effective interfacial area per molecule (a_o)
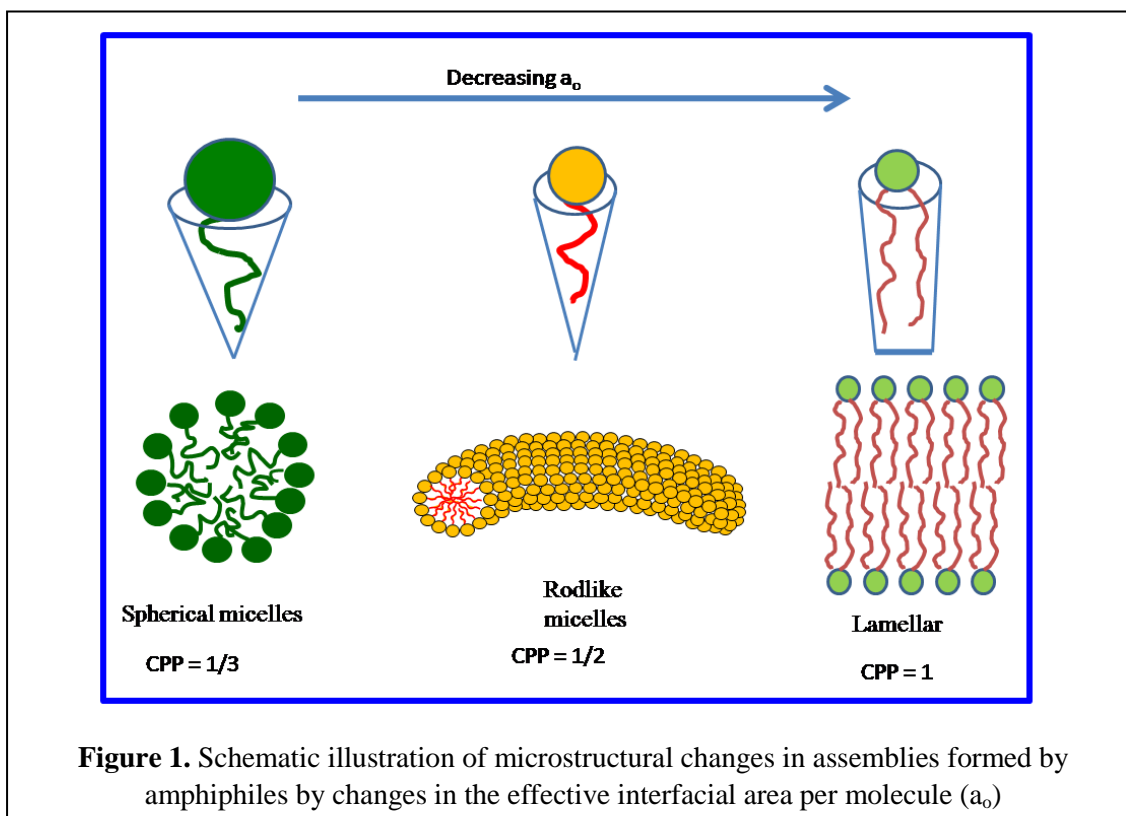
From simple geometrical calculations, it can be shown that for a spherical micelle, the optimum value of packing parameter is 1/3, and for an infinitely long cylinder it is 1/2 while for a flat monolayer or bilayers it is 1. By judicious changes in the experimental conditions or amphiphile synthesis, it is possible to modulate the microstructure of the assemblies from micelles, polymer-like micelles, vesicles, microemulsions etc. Schematic illustration of modulating the microstructure of assemblies from spheres to bilayers by changes in CPP is shown in figure 1. The structural evolution in micelles from spheres to rods, worms and vesicles have been satisfactorily explained on the basis of the CPP model, in a wide variety of systems. For example, common, single chain amphiphiles such as Sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB) etc. form nearly globular micelles close to the critical micelle concentrations (CMC). However, with an increase in surfactant concentration or addition of electrolytes, a sphere to rod transition in the micelle structure was observed. For these surfactants, the presence of both steric and electrostatic repulsion of the head groups makes the effective area large and structures with low CPP is preferred near the CMC. With the addition of electrolytes, the ionic strength of the medium increases leading to a decrease in the Debye screening length and hence reduces the electrostatic repulsion. This in turn will decrease the a_0 and rod like structures will become preferred. Recently, self assembly of surfactants has also been reported in supercooled melts, using all solid ingredients. This is an important discovery in which molten organic solids are used as a medium for micellization. These micelles could be cooled down to room temperature without phase separation leading to jammed micelles in a supercooled state. Unlike micelles in conventional solvents, these micelles are dynamically arrested, as revealed from dynamic light scattering studies. These micelles are structurally analogous to those observed in other solvents. Since the global motion of these micelles could be arrested, this will pave way for investigating micellization and its application in material synthesis. Arresting the diffusion of micelles and micro-emulsion are of great relevance in controlling the agglomeration of nanoparticles prepared in them. Figure 2 shows schematic illustration of the formation of supercooled micelles in glucose-urea melt.

Liposomes are another class of materials that attract considerable attention in drug delivery. They have shown promising results due to their ability to penetrate through leaky vasculature and
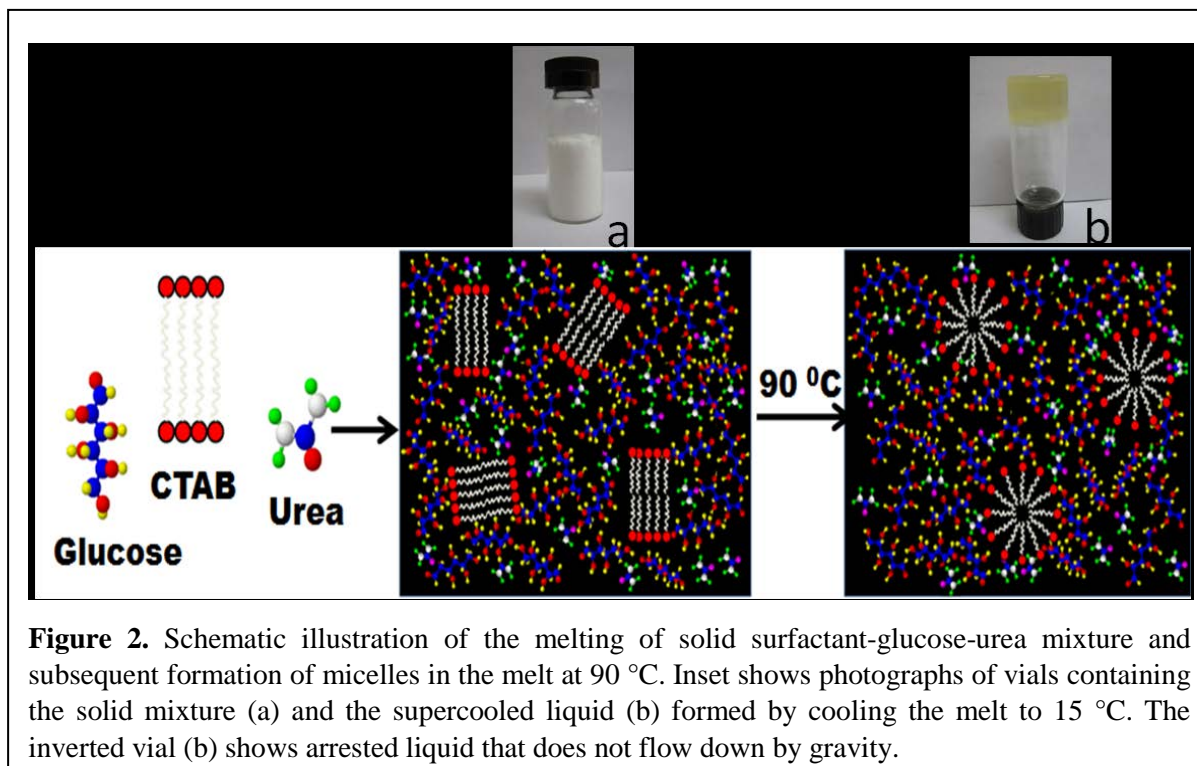
Figure 2. Schematic illustration of the melting of solid surfactant-glucose-urea mixture and subsequent formation of micelles in the melt at 90 °C. Inset shows photographs of vials containing the solid mixture (a) and the supercooled liquid (b) formed by cooling the melt to 15 °C. The inverted vial (b) shows arrested liquid that does not flow down by gravity.

alter pharmacokinetics. PEG coated vesicles with controlled particle size can be developed by cooperative assembly of block copolymers and phospholipids. The doxorubicin formulation produced using such vesicles show comparable efficacy to that of marketed drugs with covalently linked PEG coating. Self assembly approach offers a cost-effective route for the production of such complex drug delivery systems.

Nanostructure control using soft matter

Self assembly plays a crucial role in controlling the nucleation and growth of many inorganic materials. Stabilization of colloidal dispersions against aggregation is important for many practical applications. This can be achieved either by electrostatic repulsion of the charged colloidal particles or by steric stabilisation. For charge stabilisation the surface charge of the particles has to be high enough to overcome the van der Waals attractive interactions. Steric stabilisation can be achieved by attaching long chain molecules to the surface such that it creates a repulsive force between the particles by interpenetration of the chains.

Adsorption of amphiphiles at the interface of polar solids surfaces are known to create closely packed monolayers via self assembly. Such monolayer formation is sensitive to experimental conditions and often a controlled pH is necessary to form chemisorbed species. Physisorbed monolayers can be produced by Langmuir-Blodgett deposition of amphiphiles from air-water interface to a solid support. Chemisorbed monolayers have been reported over a wide variety of substrates and the nature of the functional group required for binding depends on the material of choice. Self-assembled monolayers (SAMs) on gold surface mediated by long chain alkane thiols represent one of the well studied systems. The Au-thiol chemistry has been exploited in the production of size controlled gold nanoparticles due to excellent ability in surface passivation. Octadecyltrichlorosilane (OTS) is another well known molecule that can form SAMs on silica surface. Long chain carboxylic acids are used in the production of hydrophobic coatings on substrates like alumina and Fe_2O_3. The nature of bonding between carboxylic acids and metal atom can be accessed from IR spectral studies. The chemisorption of the carboxylate moiety can be either through monodentate, bridging bidentate or chelate bidentate route.

Figure 3. Schematic of peptide mimic dendrimer coated magnetic nanoparticles
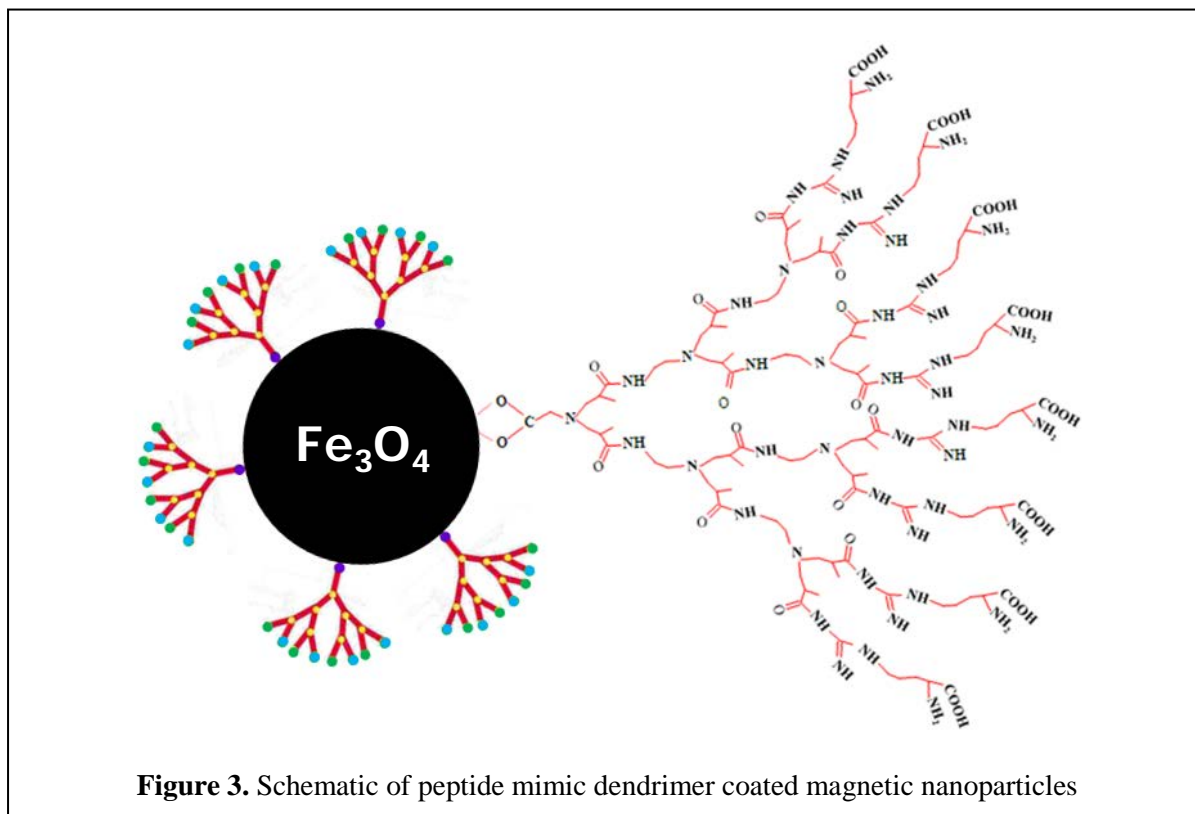
Surface functionalised Fe_3O_4 nanoparticles with good colloidal stability, protein resistance characteristics and room temperature superparamagnetic behaviour can be prepared by such soft-chemical approach. These particles show excellent heating efficacy under AC magnetic field, high loading affinity for positively charged anticancer drug, doxorubicin and sustained drug release in acidic environments. Chemisorption of amino acids such as glycine can be employed for the surface passivation of magnetic nanoparticles or hydroxyapatite nanoparticles using carboxyl moiety. Further functionalisation of the amine groups with appropriate moieties permit creation organic-inorganic structures with desired functionality. Figure 3 shows a schematic of the glycine passivated superparamagnetic nanoparticles and its further peptide mimic coating via dendrimer growth. Preparation of nanoparticles in the mesostructures of surfactant fluids offer attractive route to control the morphology of the particles.

In summary, by judiciously tuning the intermolecular interactions, self assembly can be exploited for creating diverse microstructures and its applications in functional materials. In particular polyethylene glycol functionalized carriers for non-covalent binding of drugs or proteins can be developed for cancer therapy. Stimuli sensitive assemblies that can reversibly associate or dissociate in response to environmental changes can be developed using soft matter, as model system for self regulated drug delivery vehicle. Supercooled soft matter systems can be developed using all solid ingredients and could open a new area in scientific research with potential applications. Formation of 2-D assemblies at the interface of inorganic particles can be explored to create organic-inorganic composite materials for cancer therapeutics.

Acknowledgements

Prof. P. A. Hassan joined Bhabha Atomic Research Centre (BARC), Mumbai in 1993 and presently serving as Head of Nanotherapeutics and Biosensors Section, Chemistry Division, BARC. He is honorary Professor of Chemical Sciences at Homi Bhabha National Institute. He was a visiting researcher at the University of Louis Pasteur, Strasbourg, France in 1995. He pursued his post-doctoral research at the Department of Chemical Engineering, University of Delaware, USA in 2000-2002. He has visited advanced neutron scattering facilities like National Centre for Neutron Research, NIST, Maryland, USA and Institute Lau Langevin, Grenoble, France. He has co-authored more than 190 papers in peer-reviewed journals (with h-index 48 as per google scholar), 11 book chapters and one Indian patent. His current research interests include microstructure and dynamics of self assembly, polymers, polyelectrolyte-surfactant interactions and nano drug delivery systems.

He is an elected fellow of the National Academy of Sciences, India. He is serving as the Associate Editor of Bulletin of Materials Science (Springer). He has received the Group Achievement Award by the Department of Atomic Energy (2017) and Prof. J. N. Mukherjee Memorial Lecture Award by the Indian Chemical Society (2021).

Soft chemical synthesis of functional micro-nano structures

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Multi-component heterogeneous systems consisting of both nano and micron sized structures, exhibit diverse properties and functions owing to synergistically enhanced physicochemical properties of individual components. In such materials (composites) both nano and micro structured architectures coexist and interact at the molecular/atomic levels. Devices made from the above mentioned materials are potential alternatives to thin film and bulk optoelectronic devices as they offer improved light matter interaction, better carrier transport and mechanical flexibility. Improved light-matter interaction in nano-micro structured materials is due to the enhanced absorption of light brought about by the internal reflections and reduction in the reflection losses. High surface to volume ratio of nano-micro structures facilitate creation of high concentration of charge carriers upon interaction with light. Tunable morphology and crystallographic orientation helps to achieve better charge carrier transport properties. Synthesis methods used for preparation of such nano-micro structured materials play a pivotal role in achieving desired size, shape, morphology and crystallographic orientation and associated properties. Improved optical properties arising from such materials can also be explained based on difference in the density of states brought about by the variation in their structural architecture.

For development of micro-nanostructured devices with optimum performance characteristics, it is absolutely necessary to have synthesis methods which can result in high quality nanoand microcrystals. There are large number of methods available for the synthesis of single crystalline materials with nano size dimensions. These include co-precipitation methods in presence of coordinating ligands, solvo or hydrothermal techniques, precursor decomposition, template assisted synthesis etc. For micro-crystals, techniques such as pressure-assisted space-confined methods, laser trapping, controlled inverse temperature crystallization (ITC) and hot injection methods are extensively used for the synthesis. It may be noted that the conventional methods such as Bridgman and the Czochralski (CZ) methods lead to the formation of crystals in bulk size and cannot be adaptedfor the fabrication of micro crystals. Some of the above mentioned methods will be discussed in the present talk. Various factors that influence and control the product properties obtained via these routes shall also be discussed.

Synthesis of micro-crystals

Micro-crystals are single crystals with micron size dimensions and can be seen only through a microscope and possess all the properties of bulk crystals. Micro-crystals of various sizes, shapes and morphologies can be prepared by using organic molecules like poly(4-styrenesulfonate) (PSS), which is also known as a shape control agent. Sodium salt of PSS (sodium poly(4-styrenesulfonate)), which is soluble in water, is an example of a shape control agent for the synthesis of lanthanide fluoride micro-crystals of various shapes. Wang et al. [1] synthesized $NaYF_4$ micro-crystals with a variety of morphologies, such as microspheres, hexagonal prisms, micro-tube and octahedron, by varying the concentration of PSS, pH, reaction time etc. From the studies it is established that PSS can be effectively employed as a suitable moleculefor the fine control of shape/morphologyof synthesized micro-crystals. Concentration of PSS in the reaction medium has also been found to influence the cubic to hexagonal phase transition of $NaYF_4$ crystal in addition to control of morphology or shape. Organic molecule such as ethylene glycol is also known to act as structure directing agent for the synthesis of transition and main group metal oxides of different morphologies

Similar to hydrothermal methods, spin coating combined with heating can also be used for preparation of micro-crystals with specific crystallographic orientation or face oriented micro crystals. In this method, a solution containing the dispersed nanoparticles or layered materials such as MoS_2, is placed on the chuck and the same was subjected to rotation and heating. Both temperature and centrifugal force are responsible for growth of crystallographically oriented micro-crystals by this method. A variety of halide perovskite micro-crystals with specific crystallographic orientation has been synthesized by this method.

Polyol synthesis of plasmonic nanoparticles (metal and semiconductor)

Among the many nano-micro structured composites, one of the components generally present along with micro crystals is metal or semiconductor nanoparticles. Metal and semiconductor nanoparticles in such system can be prepared by different methods and among them polyol technique is quite popular and promising. Polyols act both as stabilizing ligand and a weakly reducing agent slightly above room temperature. This property is used to reduce metal cations to form metal nanoparticles with suitable surface functionalization. Polyol technique can also be used for the synthesis of nano-micro composites mentioned above. Alternatively, the nano-size materials which are synthesized by polyolmethod find applications in the area of photo catalysis, lithium-ion batteries, fuel cells, thermoelectric generators, etc. For less noble metals, polyol synthesis is more challenging because of the lower electrochemical potential. For example in diethylene glycol medium, Indium (In^0) nanoparticles with effective size in the range of 10-100 nm can be prepared by using $NaBH_4$ as a reducing agent for In^{3+} slats [2]. The Plasmon resonance is observed for these nanoparticles and the color of the smallest particles is brownish red [2]. Initially indium salts were heated at 100°C in diethylene glycol (DEG) medium and then $NaBH_4$ solution was added to the reaction medium. The metal nanoparticles formed undergo quick aggregation to a relatively large size of around 38 nm with wide size distribution. DEG act as a solvent as well as a co-stabilizer for hydrophobic metallic surface. Due to the presence of water, In^0 nanoparticles undergo oxidation slowly to form a black coloured solution. In a similar way nanoparticles of transition metal alloys such as Ni-Fe can also be prepared (Figure 1).
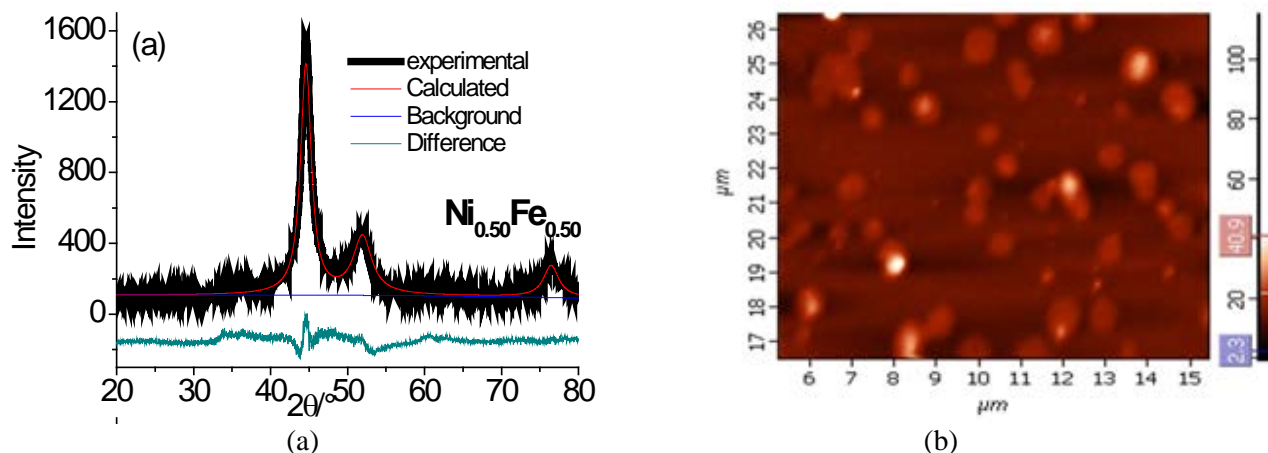
Figure 1. XRD (a) and AFM image (b) of $Ni_{0.5}Fei_{0.5}$ nano-alloy. The nanoparticles were prepared by polyol method using ethylene glycol as a solvent.

Polyol Synthesis of Oxide Nanoparticles

Polyols are ideal medium for the synthesis of oxide nanoparticles due to its water-compatible and chelating abilities. Simple metal-salt precursors like halides, nitrates, acetates etc. are used as starting materials in polyol method. Instant coordination of polyols at the surface of nanoparticles leads to excellent control in particle size, size distribution and extent of agglomeration. In addition to this, easy removal of

un-reacted polyols which are not coordinatedon the particles, after the reaction, makes the synthesis relatively simple [2]. For the preparation of oxides, presence of water is essential as it controls reaction-time, concentration and selectivity in precursor formation. The amount of water can be varied by using intrinsic condensation of the polyols (for low H_2O concentrations), by using hydrates as the starting materials (for medium H_2O concentrations), or by adding water externally (for high H_2O concentrations). The particle size typically depends on the solubility of respective precursor salts in polyol. Typically, polyol synthesis results instable colloidal suspension of almost non-agglomerated nanoparticles (1 to 200 nm in size). An important property of polyols relevant to the synthesis of oxide nanoparticles is related to its high boiling point. Thus, highly crystalline oxide nanomaterials can be obtained directly from liquid phase without implementation of any thermal post-sintering of powders [3,4]. A variety of oxide nanoparticles can be synthesized via polyol method, including various compositions, shapes, different types of dopants etc. Polyol synthesized oxide nanoparticles find different applications that include photocatalysis (e.g., Cu_2O, ZnO, $BiVO_4$), sensors (e.g., with Fe_2O_3, CuO), dye-sensitized solar cells (e.g., ZnO, TiO_2), etc.

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Phase diagrams for material synthesis

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Synthesis of materials of desired purity is one of the major challenges for the material scientists.Thermodynamics dictates that it is impossible to synthesize a pure material. In view of this, one needs todesign a chemical reaction with utmost care and choose the best possible synthesis protocol to prepare a high pure material. The selection of a suitable method of synthesis is therefore, crucial. It involves a thorough knowledge on chemical reactivity of the reactants, detail experimentation procedure, and also on understanding of the thermodynamic stabilities of both reactant and products. Depending on the reaction mechanisms and nature of the reactants and products, a number of reaction protocols may be possible for the synthesis of a given materials. One needs to choose the most appropriate synthesis protocol judiciously, which will yield high pure products with less number of steps and economically.

The solid-state reactions can be categorised into redox reactions, thermal decomposition reactions, combustion reactions, hydrothermal synthesis, substitution reactions, diffusion-controlled reactions etc.Various synthesis methods have been developed based on the above types of reactions to synthesize wide range of materials with tailored properties for specific applications. Depending on the material properties of reactants and products, different synthesis approaches are adopted. Mechanical mixing of the reactants followed by heat induce chemical reactions and co-precipitating precursors from a solution followed by heating the precipitates are the most commonly employed solid state synthesis methods. Hydrothermal method is another simple low temperature synthesis procedure, where the reactants are heated in a closed vessel containing water under high pressure and temperature to facilitate solid-state reactions. Sol-gel is yet another synthesis method, where a colloidal suspension (sol) is converted into a gel and subsequently dried to form a powder, which is auto ignited to form the products having high surface area. In Chemical Vapor Deposition (CVD) method gaseous reactants are deposited on heated substrate to form a product, whereas in the flame pyrolysis method the precursor materials are introduced into a flame, where they react and form solid particles. A dense, solid material is formed by the Spark Plasma Sintering (SPS) process where reactant powders are subjected to a combination of pressure and high temperature. In high-pressure synthesis method a Diamond Anvil Cell (DAC) is used, where reactants are subjected to extremely high pressures in a small chamber to induce solid-state reactions. For the synthesis of alloys high temperature synthesis methods like arc melting, induction melting and electron beam melting, laser heating etc. are used under controlled atmosphere.

Synthesis of material following above methods always requires *a priori* knowledge of the chemical reaction including the composition, crystal structure, and the properties of the product. Understanding the thermodynamics of the chemical reactions, such as stability of the reactants and products under various conditions, formation energies of intermediate species and kinetics of transformation are important for the successful synthesis of pure material. Appropriate reaction conditions such as temperature, pressure, atmosphere and reaction time, etc., must be maintained during the reaction. In addition, care must be taken to choose a suitable chemical precursor or starting materials that can easily react to form the desired product.

It is observed that even after taking necessary precautions, the products are often formed with undesirable impurities, which may alter the properties of the material. These impurities are introduced into the final product through various mechanisms. The products can have impurity phases such as residual reactants, formation of undesirable compounds, non-stoichiometric compounds, substitutional solid solution, inclusions, surface impurities and contaminations, oxide impurities, decomposition by-products etc. In addition, the product phases can have intrinsic point defects such as vacancies,

interstitials, Frenkel defects, Schottky defects; extrinsic point Defects like doped material, substitutional impurities, interstitial impurities, crystallographic impurities like polytypes, polymorphs etc. Controlling and minimizing the formation of these impurities is essential in solid-state reactions to achieve the desired material properties. Careful selection of reaction conditions, purification methods, and post-processing steps can help mitigate the presence of impurities in the final product.

It is therefore obvious to ask how to synthesize a material containing minimum amount of impurity and how to predict the best synthesis approach. The question is quite pertinent for young researchers and students who do not have sufficient experience on material synthesis approaches. Predicting and optimizing synthesis conditions for inorganic solids is however quite complex, that requires long experience in experimentations. Although there exist some thumb rules for the synthesis of material, however no single method can be applied to synthesize two different types of reaction. It is always advisable to look into thermodynamic information of the system of interest like melting temperature, boiling temperature, heat capacity, enthalpy of formation and free energy data to fix the reaction conditions and to predict the feasibility of a given reaction. However, thermodynamic calculations will not throw light on kinetics of chemical reaction and most suitable route for the synthesis of a product. Moreover, thermodynamic data base for the reactants and products may not always be available to calculate the equilibrium constant and temperature, pressure conditions for the reaction.

Phase diagrams lay foundation for exploring new materials, where different compositions and processing conditions are explored to discover new materials with unique properties. Phase diagrams are incredible tools in material science for guiding the synthesis process, enabling the design of new materials and helping researchers understand the relationships between temperature, composition, phase stability and plays a crucial role in advancing materials technology and innovation. Phase diagrams prove handy in the identification of phases coexisting under a given condition of temperature, pressure and composition. It helps in optimizing the synthesis condition for a specific material and designing of alloys with desired mechanical, electrical, or thermal properties. They assist in controlling defects in materials. For example, in semiconductor manufacturing, phase diagrams help determine the right conditions for minimizing crystal defects and enhancing electronic properties. They also provide insights into phase transformations, such as melting, solidification and phase transitions. This understanding is crucial for predicting material behaviour during processing and service. For critical applications where impurities or unwanted phases can lead to material failure, phase diagrams are used to minimize the formation of undesired phases during material synthesis.

Examples of some specific applications of phase diagram in the material synthesis and processing are given below.

1. **Alloy design:**
   One of the earliest uses of phase diagram is age-hardening of alloys, i.e. copper-aluminium alloy, where a precipitation of a second phase hardens an alloy. Age hardening has led to development of several families of commercial alloys. Phase diagram predicts the conditions under which precipitation of hardening phase takes place.

2. **Development of Austenitic Stainless Steel**
   Phase diagram predicts that it is possible to use manganese and aluminium as substitute for nickel and chromium in stainless steels. From the phase diagram of Mn-Fe and Al-Fe, it is possible to predict that manganese should be capable of replacing nickel as it stabilizes the γ-iron phase (austenite), and aluminiumcan substitute for chromium because it stabilizes the α-iron phase (ferrite), leaving only a small γ loop (Fig. 1a and b). The phase diagrams of Fe-Cr, Fe-Al, Fe-Mn and Fe-Ni binary stems are show in Fig 1 and 2.
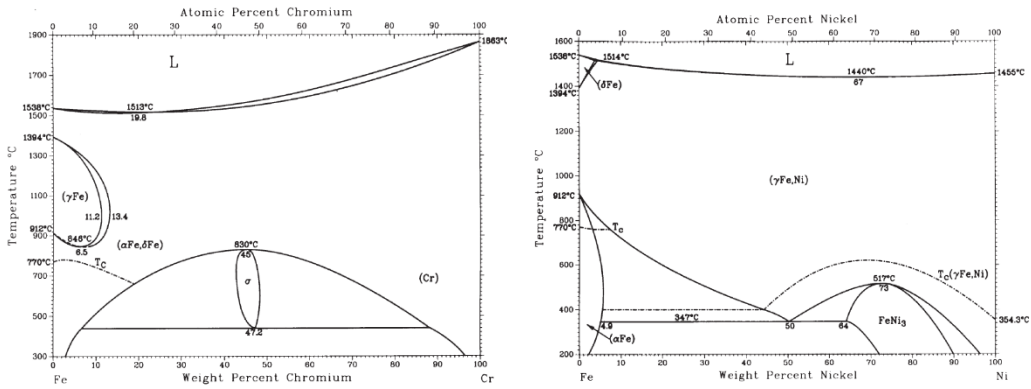
Fig. 1(a, b) Two binary iron phase diagrams, showing ferrite stabilization (iron-chromium) and austenite stabilization (iron-nickel).
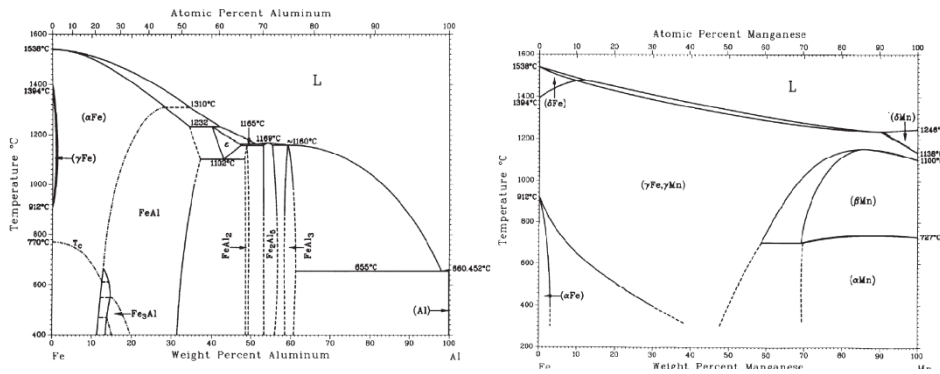
Fig.2 The aluminium-iron and iron-manganese phase diagrams.

3. **Hardfacing:** Nickel-base hard facing alloy used for corrosion and wear resistance is prepared based on the phase diagram information. Alloy samples with acceptable range of total chromium borides and chromium matrix are synthesised based on B-Cr-Ni phase diagram. The alloy is then fine-tuned for the composition to ensure fabricability of welding rods, weldability, and the desired combination of corrosion and abrasion properties.

a. **Carbide Cutting Tools**: In manufacturing of carbide cutting tools the serious problems of brittleness of the sintered carbide are solved with help of phase diagram information of the systems. The compositions for cobalt-bonded sintered carbides are shown in the shaded area of the ternary phase diagram in Fig. 3, along the dashed line connecting pure tungsten carbide (WC) on the right and pure cobalt at the lower left.
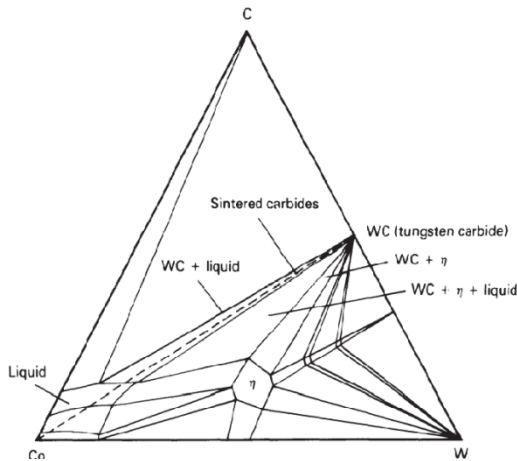
Fig. 3 Co-C-W phase diagram

At 1400 °C, materials with these compositions consist of particles of tungsten carbide suspended in liquid metal. However, when there is a deficiency of carbon, compositions drop into the region labelled WC + η + liquid, or the region labelled WC + η, where tungsten carbide particles are surrounded by a matrix of η phase. The η phase is known to be brittle. The upward adjustment of the carbon content by only a few hundredth of a weight percent eliminate this problem.

There are numerous examples of application, where phase diagrams have been successfully applied to synthesis various products of desired properties. There are no doubts that phase diagram is one of the most important tools for material fabrication and material engineering. However, the information derived from phase diagram do have certain limitations. Some of the limitation of phase diagrams in material synthesis are given below.

1. Phase diagrams gives idea about the phases that coexist with each other at given condition of temperature, pressure and composition under equilibrium conditions. It does not elaborate about kinetics of formation of these phases. However, in normal cases materials are rarely formed under perfectly equilibrium condition. There will always be certain degree of non-equilibrium condition.

2. Phase diagrams is silent about character of the transformations and possibility of suppression of crystallographic transformation. It does not tell about the rate of heating/cooling to avoid the transformation.

In view of limitations of thermodynamics and phase diagram information, predicting the method of synthesis of materials is not always straightforward. Synthesis of pure new material requires elaborate experimentation to fine-tune the process. Collaboration with experienced researchers in the field can be highly beneficial, especially when working with less well-studied materials or when attempting to optimize synthesis conditions.

Dr. Ratikanta Mishra received M.Sc in Chemistry from Utkal University, Bhubaneswar and joined the BARC as a Scientific Officer from 36th batch of BARC Training School. Presently he is heading Thermodynamics and High Purity Material Section of Chemistry Division, BARC. Dr. Mishra is an expert in thermal analysis and chemical thermodynamics. He has made major contributions in the field of chemical thermodynamics of nuclear materials relevant to Indian Nuclear Programs, which include development of thermodynamic data base for Advanced Heavy Water Reactor (AHWR) Nuclear Fuel systems, high temperature chemistry and thermo-physical properties of Molten Salt Breeder Reactor (MSBR) fuel systems.
He has successfully led a team to synthesize ultra-pure materials for strategic applications. Dr. Mishra has developed new high temperature lead free nano-solder materials. He has published more than 175 research papers in peer reviewed international journals, several book chapters and review articles.
Dr. Mishra is the recipient of Netzsch ITAS award, Marie Curie International Fellowship and Alexander von Humboldt Fellowship.

Synthesis *via* Ionic Liquids: A Green Route to Sustainable Materials

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Lanthanide (Ln^{3+}) ion(s)-doped or rare-earth ion(s) doped nanomaterials have been considered as a very important class of nanophosphors for various photonic and biophotonic applications. Unlike semiconductors and organic-based luminescent particles, the optical properties of Ln^{3+}-doped nanophosphors are independent of the size of the nanoparticles. However, by varying the crystal phase, morphology, lattice strain etc. of the host materials along with making core-shell structure; relaxation dynamics of dopant Ln^{3+} ions can be effectively tuned. Interestingly, a judicious choice of dopant ions leads to unparallel photophysical dynamics like quantum cutting, upconversion, energy transfer, etc. Recently Ionic Liquids (ILs) have drawn a tremendous attention in the field of nanomaterials synthesis due to their unique properties like negligible vapour pressure, non-flammability and most importantly their tunability etc; for which these are oftenly called "green" and "designer" solvents. Different aspects of ILs like their ability to work as a templating agent, solvent, reaction partner and sometimes their use as a "three in one" in nanomaterials synthesis will be highlighted along with various photoluminescence mechanisms of Ln^{3+}- ion like up- and down-conversion (UC and DC) and their various photonic and biophotonic applications.

What are ionic liquids: past and present scenario?

ILs are now a very important part of chemistry, materials science, electrochemistry and recently, it has got tremendous attention for several applications due to their tunable properties. Ionic liquids (ILs) are organic salts, which have melting point less than 100 °C in ambient condition and generally comprised of cation and anion.[1-7] Therefore, many combinations (maximum 10^{18}) of cation and anion are possible leading to the formation of variety of ionic liquids. Besides this, different types of IL cations can also be produced by substituting with the desired alkyl chain length on the

Figure 1. Ionic liquids (ILs) toolkit consists of cations and anions.[2]

fundamental cations such as imidazolium, pyridium $[C_5H_5NR]^+$, pyrolidinium $[C_5H_{10}NR_2]^+$, phosphonium $[PR_4]^+$, sulphonium $[SR_3]^+$, alkylammonium $[NR_1R_2R_3R_4]^+$ (here R_1=-H, alkyl and $R_{2,3,4}$= alkyl groups) etc. In addition, by changing the anions such as X^- (Cl^-, Br^-), BF_4^-, PF_6^-, OTf^-, RSO_4^-, OH^- and so on, one can get IL with different properties (see **Figure 1**).[2] As a result of these incredible characteristics of the ILs, chemical and physical properties can be feasibly tuned according to the necessity of reaction conditions and for those reasons ionic liquids are often called as '*designer*' solvent.[2]Actually ILs came into picture a century ago; when ethlyammonium nitrate salt got recognition as molten salt.[2]Application of ionic liquids was assured when pyridinium salt was used for dissolution of cellulose at 100 °C.[2] Then, for reprocessing the nuclear fuel, low melting temperature chloroaluminates ($AlCl_4^-$) based ionic liquid was used.[2]Due to its important properties, ionic liquids are recently used in nanomaterials synthesis and various techniques for example, IL assisted hydrothermal, solvothermal, microwave synthesis, sonochemical techniques are used to prepare range of materials like oxides, sulphides, fluorides, phosphates, rare-earth doped materials etc

(**Figure2**). In all these cases ILs are not only used as a templating agent, solvent but also as a reaction precursor.

Intrinsic properties of ILs which helps in nanomaterials synthesis

The effects of tunable properties of ILs are significantly observed on the crystal phase, host matrix, controlling the size, modification of morphology.[1-7] In this way, by controlling all these structural properties of Ln-doped nanocrystals, optical properties of the dopant ion can be judiciuosly tuned.

Reaction medium and capping/templating agent

In the beginning, ILs were used as reaction medium for synthesizing the inorganic nanomaterials especially lanthanide-based nanomaterials. Distinctive features of ILs like high thermal stability, negligible vapour pressure, broad liquidus range and most importantly adjustable properties makes them far better than conventional molecular liquids. The negligible vapor pressure of ILs can be estimated by enthalpy of vaporization and its magnitude for ILs is much higher than the conventional liquids.[2]These features of ILs increase their potential for the reaction medium.

Figure 2. Scheme represents the role of ionic liquids in synthesis of various classes of nanomaterials.[2]

Tuning the crystal phase and size of the host materials

Tuning of crystal phase of the nanomaterials is state of the art approach which is substantially dependent on the various factors such as nature and viscosity of reaction medium, surfactants, varying of reaction temperature and so on.[1-7] Amongst them, reaction medium and its concentration have pivotal influence in tuning the crystal phase of nanoscale particles via controlling the kinetics of reaction. For example, phase tuned quantum confined In_2S_3 nanocrystals are accessible solvothermally using task-specific ionic liquids (ILs) as structure directing agents.[6] Selective tuning of size, shape, morphology, and, most importantly, crystal phase of In_2S_3 is achieved by changing the alkyl side chain length, the H-bonding, and aromatic π-stacking ability of the 1-alkyl-3- methylimidazolium bromide ILs, [$C_n$mim]Br (n = 2, 4, 6, 8, and 10). It is observed that crystallite size is significantly less when ILs are used compared to the synthesis without ILs keeping the other reaction parameters

Figure 3. Indium sulphide nanoparticles via ionic liquids and its catalytic/photocatalytic properties.[6]

the same. At 150 °C, when no IL is used, pure tetragonal form of β-In_2S_3 appears however in the presence of [$C_n$mim]Br [n = 2,4], at the same reaction condition, a pure cubic phase crystallizes (**Figure 3**). However, in case of methylimidazolium bromides with longer pendant alkyl chains such as hexyl (C6), octyl (C8) or decyl (C10), nanoparticles of the tetragonal polymorph form. Similarly Oxygen-free, Eu^{3+}-doped $NaGdF_4$ nanocrystals with high quantum cutting efficiency are accessible at low temperatures (room temperature to 80 °C) using task-specific ionic liquids (ILs) as structure directing agents and only water as solvent.[1] Selective tuning of the shape, morphology and, most

importantly, the crystal phase of the host lattice is achieved by changing the alkyl side length, the H-bonding capabilities and the concentration of 1-alkyl-3-methylimidazolium bromide ILs, $[C_n mim]Br$. When using $[C_2 mim]Br$, hexagonal $NaGdF_4$ nanoparticles are obtained. In the case of methylimidazolium bromides with longer pendant alkyl chains such as butyl (C4), octyl (C8) or decyl (C10), extremely small nanoparticles of the cubic polymorph form, which then convert even at room temperature (RT) to the thermodynamically favoured hexagonal modification. To the best of our knowledge, this kind of spontaneous phase transition is not yet reported. The hexagonal nanomaterial shows a substantial quantum cutting efficiency (154%) whilst in the cubic

Figure 4. Quantum cutting materials for energy saving.[1]

material, the effect is negligible (107%). The easy yet highly phase selective green synthesis of the materials promises large scale industrial application in environmentally benign energy efficient lighting (**Figure 4**).

Ionic liquids as reaction partner

Another important feature of ILs is their use as reaction partner or precursor. This characteristic of ILs makes them much superior than other traditional molecular solvents. For this, all credit is given to the tunable properties of ILs especially anion counter ions. By varying the anion part of ILs, different reaction partner can be designed according to the desired product.[2] For example, we have developed a phase pure, cubic, up-converting $BaGdF_5$:Er/Yb doped nanocrystals accessible via $[C_4 mim]BF_4$ ionic liquids where ILs are working as solvent, templating agent and

Figure 5: Upconverting materials for increasing efficiency in DSSC devices.[3]

reaction partner by releasing the fluoride ion.[3] Then $BaGdF_5$:Er/Yb doped nanocrystals which worked as a " spectral converter" are combined with TiO_2 to apply as absorption layer in a dye-sensitized solar cell (DSSC) as a potential technology to harvest solar energy. Bright-green (520 and 540 nm) and red (665 nm) emission were observed due to the transitions of $^2H_{11/2} + {}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. Under one sun illumination, cells fabricated with $BaGdF_5$:Er^{3+}(1%)/Yb^{3+}(10%)/TiO_2 absorption layer showed highest photon conversion efficiency (PCE) of 7.75 % with current density, J_{sc}=15.9 mA/cm². However, when only TiO_2 is used as absorption layer, a much lesser PCE of 4.60 % along with J_{sc}=9.6 mA/cm² are obtained (**Figure 5**).

Figure 6: Schematic diagram of BaF_2-GO nanocomposites and their applications.[7]

Recently a tremendous interest has been created on graphene oxide-based nanocomposites (NCMs) which exhibit diverse photonic and bio-photonic applications. An innovative nanoengineering using a task specific ionic liquid (IL), 1-butyl-3-methyl tetrafluoroborate $[C_4 mim][BF_4]$ allows to access a unique class of luminescent nanocomposites formed between

lanthanide-doped binary fluorides and graphene oxide (GO). Here, the IL is used as a solvent, templating agent and as a reaction partner for the nanocomposite synthesis i.e., "all three in one".[7] Our study shows that GO not only controls the size of the nanocomposites (NCMs), however it can tune the luminescence properties too. For example, excitation spectra of Ce^{3+} is higher energy shifted when GO is attached. In addition, magnetic properties of GdF_3:Tb^{3+} nanoparticles (NPs) and GdF_3:Tb^{3+}-GO NCMs are also studied at room temperature (300 K) and very low temperature (2 K). High magnetization results for the NPs (for example 6.676 emu g^{-1} at 300 K and 184.449 emu g^{-1} at 2 K in the applied magnetic field +50 kOe to -50 kOe) and NCMs promises their uses in many photonic and biphotonic applications including MRI imaging etc.

In summary, ionic liquids have tremendous potentials for nanomaterials synthesis with diverse range of applications. ILs can be used not only as a template, solvent but also as a reaction precursor. Augmenting the fascinating properties of ionic liquids, lanthanide doped nanomaterials, nanocomposites can be prepared with aiming different applications like quantum cutting for energy efficient and environmentally benign lighting, enhancing efficiency in solar cells etc.

Acknowledgment

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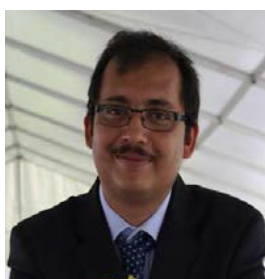
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Metallic Alloys and Intermetallics: Synthesis Methodologies

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The modern era of global technological evolution, has at its core, an unprecedented development of materials, brought out through innovative advancement in materials preparation and characterization methodologies. At ambient conditions of temperature and pressure, materials around us can broadly be categorized as (i) metals, alloys and intermetallics, (ii) ceramics and glasses, (iii) polymers and elastomers and (iv) composites. A quick look at materials around us enables to appreciate the relevance of above categories. Among these, metallic alloys and intermetallics can be considered as one of the greatest gift of chemistry (and metallurgy) to the mankind. General definition of metals, alloys and intermetallic compounds, with examples, will be introduced to begin the workshop lecture.

It is interesting to note that pure metals have limited usages, which expand enormously upon alloying. From sewing needles to a screw/nail, which are widely used in our day-to-day lives, applications of alloys and intermetallics span over almost everything from automobiles to aviation industry, structural civil engineering to heavy industries, microelectronics to nano-engineering, etc. The science of mixing multiple metals (or even metals with non metals) to obtain variety of alloys and intermetallic compounds is quite fascinating and provide ample opportunities to chemists / metallurgists to develop new / modified alloys and intermetallics. Synthesis of these materials is governed by (a) fundamental aspects such as chemical thermodynamics and equilibrium phase diagrams of the constituents and (b) process variables such as temperature, pressure, irradiation, metallurgical working, etc. By primarily influencing the kinetics of formation, different process variables yield end-products with vividly distinct properties. It is therefore essential for researchers engaged in this field to be aware of various synthesis methods for preparation of metallic alloys and intermetallic compounds and essential experimental precautions to be followed during synthesis. The lecture would outline a few of these synthesis methods at lab-scale with simple examples and scientific / practical basis for the choice of method(s).

For synthesis of bulk alloys / intermetallics, two approaches are generally followed namely, melt-cool formation and solid-state reaction. Since most metals are miscible into each other in molten state (barring a few systems where immiscibility region exists in molten region), the melt-cool approach is widely used for preparation of metallic alloys and intermetallic compounds. It usually involves heating the constituents (metals) at temperatures higher than the melting point of highest melting constituent to allow formation of a uniform and homogenous molten metallic mix. The temperature is then lowered to allow solidification of molten mix. Depending upon the cooling rate, solid product (alloy / intermetallic phase) may be obtained in the form of amorphous alloy (bulk metallic glasses), or high temperature melt-quenched phase(s), or phase(s) governed by the equilibrium phase diagram. Following heating techniques can be used to obtain bulk molten mix of constituents:

(i) **Direct flame / furnace heating in air:** It is used to prepare metallic materials that are inert to high temperature oxidation / nitridation. Examples include Au-Ag alloys, Pt-Rh alloys, Pt-Ir alloys, etc.

(ii) **Direct flame / furnace heating under inert atmosphere:** It is employed when constituents are reactive to areal oxidation / nitridation. Materials that attain complete molten state below 1000 K are usually prepared this way. Some examples include Hg-M alloys (M = In, Sn, etc.), Na-K alloys, Al-based low melting alloys, etc.

(iii) **Arc-melting technique:** Here, constituents are kept in a dynamically cooled, electrically conducting crucible (usually copper) housed in a gas-tight enclosure having transparent viewport. Depending upon reactivity of constituents, appropriate atmosphere is maintained inside the

enclosure. An electric arc is initiated between the crucible and refractory electrode (c.a., thoriated tungsten) through low voltage high current power supply. Within few seconds, constituents melt under the arc in cooled crucible and the arc is withdrawn by terminating the power (or increasing the electrode separation). The molten mass thus rapidly solidifies to yield melt-quenched alloy, which may be annealed further to obtain equilibrium phases. Various aspects, which are useful to prepare alloys / intermetallics by Arc-melting technique, will be discussed with examples.

(iv) **Vacuum induction melting technique:** In this method, constituents to be melted are taken in a chemically compatible refractory crucible (c.a., tantalum, molybdenum, graphite, tungsten, etc.) and evacuated through water cooled gas-tight enclosure (usually quartz. A radio-frequency (RF) induction coil (copper) surrounds quartz enclosure. The RF coil, upon powered by alternating current, induces eddy current in the crucible containing the constituents. Eddy currents dissipate heat and causes melting of constituents under highly controlled atmosphere thereby enabling the synthesis of alloys / intermetallics with accurate composition control. This technique is preferred for synthesis of high temperature alloys, nuclear alloys, superalloys, etc. With the help of examples, the lecture would highlight experimental precautions that are necessary, while using this technique.

(v) **Levitation melting technique:** This technique is mostly used for phase homogenization of a pre-synthesized alloy / intermetallic by contactless melting. Herein, the charge to be melted is placed above a conducting coil carrying high frequency current. Surface currents are thus induced in the charge, which provides Lorentzian force to support it against gravity (hence levitation). Simultaneously, The Joule dissipated heat melts the charge under levitated condition. Utilization scope of this technique, with its advantages and challenges will be discussed, manly in reference to its use for fundamental studies on high purity alloys.

Other than melt-cool approach (outlined above), metallic alloys and intermetallics can also be synthesized / processed by solid-state reaction (powder processing) route. Herein, powdered reactants are uniformly mixed and compressed to obtain compacts (cold uniaxial / isostatic pressing), which have enormous intimately connected interface among the reactant particles. These compacts are heated at temperatures below the melting point of highest melting constituent (known as pressure-less sintering) or subjected to high temperatures as well as pressures (hot uniaxial / isostatic pressing). Efficient atomic diffusion through reactants' contact interfaces remains the key driving factor for alloy preparation via solid-state approach. Since powdered form of most metals / alloys is quite reactive (many times pyrophoric) under ambient air, powder handling is carried out under inert atmosphere (argon, nitrogen, helium, vacuum, etc.). Various practical aspects of this approach along with major application areas, advantages and challenges will be discussed during the lecture.

Another innovative route to prepare / process select metallic alloys (especially ceramic reinforced alloys) is via hydrogenation-dehydrogenation route. It is known that metals / alloys / intermetallics undergo pulverization upon multiple cycles of hydrogen absorption and desorption, thereby leaving a highly reactive metallic powder residue. If hydrogen used for the above purpose is mixed with trace amounts of reactive gases (oxygen / nitrogen), the resulting powders are obtained as admix of metallic particles and their ceramic forms (oxides/nitrides). High temperature of such powders (or powder compacts) under controlled atmosphere leads to formation of ceramic reinforced metallic composites that have superior mechanical properties as compared to non-reinforced counterparts. Experimental aspects of this route will be discussed during the lecture.

Other than bulk form, requirement of alloys / intermetallics in various other forms is progressively increasing. These include thin films, coatings, multi-layers and nano-structures. Novel preparative methods are needed to obtain metallic materials in such forms. Following approaches are used towards this requirement:

Vapor deposition route: It is a widely used method wherein metallic materials are deposited over a substrate (kept at pre-defined temperature) either by evaporation under low pressure-high temperature (LPHT) conditions or by dislodging (sputtering) under the impact of energetic ions (*c.a.,* argon ions) / intense laser beam (pulsed laser deposition; PLD). In case of LPHT vapor deposition, it

is desired that material (alloy / intermetallic) to be deposited has congruent melting temperature with adequate vapor pressure so that it is stoichiometrically deposited in the form of film / layer over the substrate. In case of ion-sputtering / magnetron sputtering or pulsed laser deposition, requirement of congruent melting temperature of deposition material is relatively less stringent. In case suitable alloy / intermetallic target is not available, sequential deposition of constituent metals is carried out to form metallic multi-layers. High temperature annealing of such multi-layers enables inter-diffusion of constituent metals to form alloys / intermetallics at the interface region of multi-layers. Such methodologies are widely used for design of different types of metallic contacts (Ohmic, Schottky, etc.) for applications in electronics industry. A glimpse of these synthesis methods will also be provided during the lecture along with examples.

Finally, the lecture will cover few solution-based (aqueous / non-aqueous) methodologies (with illustrative examples) for synthesis of metallic alloys / intermetallics in the form of nano-/micro-crystalline powders. These would include (i) Solution combustion synthesis of nanocrystalline metallic alloys / intermetallics under highly reducing chemical environment and (ii) Solvo-thermal synthesis of intermetallics / alloys under non-aqueous higher polyols. The lecture would conclude with mention of useful tips that would aid researchers to synthesize metallic materials with desired properties.

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Synthesis, characterization and properties of borides, carbides, nitrides and phosphides

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Abstract

Metal or non-metal borides, carbides, nitrides and phosphides have been used in many applications due to unusual properties as compared to metal or elemental B, C, N or P. The type of their chemical bonding in such system can be of ionic or covalent or mixture or metallic in nature. The stoichiometry of such system depends on method of chemical synthesis, environment, pressure, temperature, etc. This can change their properties: electrical, mechanical, magnetic and optical properties. Even in nanosize range, the shape and size of particles are important parameters in determination of properties of materials.

1. Introduction

Borides, carbides, nitrides and phosphides of metals or non-metals have been used in many areas such as catalysis, soft and hard magnetic devices, coating materials, cutting tools, magnetic sample holders [1, 2]. Boron nitrides/carbides are used as sample holders in magnetic measurement because such materials have diamagnetic property and also are stable in different environments and temperatures. Tungsten carbides have been used as cutting tools because of ultra-hard property. Silicon nitrides have been used as AFM tips. Metal borides and phosphides have been used as catalysts in various chemical reactions. TiN has been used as decorative coating material on various devices due to golden colour possessed by them. CrC and CrN have been used as coating materials to improve chemical stability of materials in harsh environment. Fe_4N and $Fe_{16}N_2$ have been used as soft ferromagnetic materials, whereas $Sm_{13}Fe_{87}N$ and $Nd_2Fe_{14}B$ have been used as had magnetic materials at room temperature to high temperature (say 500 ^{o}C). GaN, InGaN, SiC, BN and InP have been used as luminescent materials and detectors. MgB_2 and NbN have been used as superconducting wire in electronic devices.

Binary compounds of such borides, carbides, nitrides and phosphides of metals or non-metals have the chemical composition of X_aY_b (X = metal or non-metal, Y = B, C, N or P). The chemical bonding in such X_aY_b is of ionic, covalent, or mixture and metallic in nature. In some cases, covalent bonding of single, double or triple types is observed in B-B containing compounds (B-B, B=B, B≡B). Expansion of metal lattice is observed in transition metal nitrides and carbides when 1-5 at.% C or B are doped to transition metal nitrides. This is considered as interstitial nitride or carbide because of small ionic sizes (C or N) comparable with octahedral sites of transition metal lattices (TiC, VN, NbN).

The electron transport and magnetic properties of borides, carbides, nitrides and phosphides of metals or non-metals have shown dependent on amount of ratio between X and Y. For example, FeN is paramagnetic, Fe_2N is antiferromagnetic, Fe_3N are antiferromagnetic-ferromagnetic mixture, Fe_4N and $Fe_{16}N_2$ are ferromagnetic. It is expected that magnetic moment per Fe atom in $Fe_{16}N_2$ is more than that of pure bcc Fe. Electrical resistivity increases with increase of N or C in Fe (Fe_aC or Fe_aN). The superconducting transition (T_c) of NbN is more than Nb or Nb_2N. Many compounds of lanthanides and actinides have shown the interesting properties such as thermo-emission due low work function and thus, they are used as cathode materials in SEM/TEM instruments. Many examples can be mentioned: LaN, LaB_6, UC, CeP_5, CeB_6. Many compounds of p-block elements have been used as temperature stable phosphor (e. g., SiC). Even, SiC has been used as heating elements in furnaces. Materials comparable with diamond in term of hardness are found in nitrides and carbides (*e.g.*, AlN, BC, BN and C_3N_4).

Some of borides, carbides, nitrides and phosphides of metals or non-metals can be prepared in the form of powder, thin films and dispersion forms depending on requirement. Their properties are also dependent on size and shape of particles in nanosize range.

In this article, the various synthesis routes for borides, carbides, nitrides and phosphides are mentioned. This includes the preparation of bulk powder, nanosized particles, layered structure and thin film materials. Some of characterization techniques and properties are also provided.

2. Synthesis methods

The synthesis methods of material with binary composition X_aY_b (X = metal or non-metal, Y = B, C, N or P) are mentioned here [1, 2].

2.1 Synthesis methods of nitrides

2.1.1 *High temperature synthesis in N_2 or N_2-H_2*

Transition metal nitrides are prepared by heating metal powder or film in N_2 or N_2-H_2 atmosphere at 1200 ^{o}C or above this temperature. At high temperature, dissociation of N_2 into atomic nitrogen atoms takes place.VN and TiN are prepared at 1200 ^{o}C from vanadium and titanium metal and N_2 gas.

2.1.2 *High temperature synthesis in NH_3*

Many nitrides (MN) of d and f block elements are prepared by passing NH_3 over elemental power or elemental oxides or metal-ligand precursors in large temperature range 300-1000 ^{o}C. However, temperature for formation of metal nitride in N_2 is more than that in NH_3. Ammonia (NH_3) exits in gaseous state and dissociation takes places at elevated temperatures. TiN is prepared at 900°C from Ti in NH_3, whereas VN is prepared at 700 ^{o}C.

2.1.3 *Thermal decomposition of single source precursor*

Compounds having M-N linkage can produce the metal nitrides at elevated temperature. It is easy to form metal nitride. Ni_3N is prepared from $[Ni(NH_3)_6](NO_3)_2$ in NH_3 gas atmosphere at 300 ^{o}C, whereas VN is prepared from $[VO(NH_2O)_2Gly].H_2O$ at 500 ^{o}C.

2.1.4 *Use of urea/azideas source of nitrogen*

Urea ($OC(NH_3)_2$) and sodiumazides (e.g., NaN_3) are used as source of nitrogen for preparation of nitrides. In this way, carbon nitride (C_3N_4) can be prepared from urea at 400-550 ^{o}C by very slow heating (1-2 ^{o}C/min). Metal nitride can be prepared from metal powder and sodium azide at relatively low temperature.

2.1.5 *Other methods*

There are many methods to prepare metal nitrides. Some of them are (1) use of hard template having nitrogen source, (2) epitaxial growth of nanowires or nanorods on substrate, (3) CVD or PVD for thin film formation, (4) formation of single crystals, (5) formation of mesoporous metal nitrides, (6) metathesis reaction, (7) formation of layered nitrides, (8) mechanical transfer of metal nitrides grown on a substrate to another substrate, (9) formation of heterostructure types (multi-quantum wells), (10) use of high pressure and high temperature for formation of different phases of metal nitrides, (11) formation of different phases of nitrides under sudden cooling and tempering, (12), electro-chemical route, (13) use of supercritical fluid ammonia or solvo-thermal or ammono-thermal route, (14) self-propagating high temperature synthesis and (15) shape and size engineering, etc.

2.2 Synthesis methods of carbides

2.2.1 *Carbo-thermal route*

Carbides are prepared by direct heating of metal or non-metal powder or wire or metal hydride with carbon source (e.g., graphite) at high temperature (above 1000 ^{o}C) in Ar atmosphere.

2.2.2 Carbo-thermic reduction route

The meta oxides or hydroxides or carbonyl or chloride are reacted with carbon or CO with or without H_2/Ar atmosphere at elevated temperatures (above 1000 ^{o}C) to prepare carbides.

2.2.3 Carburization route

Carbides are prepared from the metal oxides or halides or non-metal with CH_4 or C_2H_6 light gas with or without H_2 gas at elevated temperatures (above 1000 ^{o}C).

2.3 Synthesis methods of phosphides

2.3.1 Metal or non-metal and phosphorus interaction

Phosphides are prepared by direction interaction betweenmetal or non-metal and phosphorus at higher temperatures (300-1000 ^{o}C) at Ar atmosphere.

2.3.2 Metal salt or complex and PH₃/H₂ mixture interaction

When metal salt or complex is interacted with PH_3/H_2 mixture at lower temperature 250 – 350 ^{o}C, it forms metal phosphide.

2.3.3 Metal salt and hypophosphite interaction

When metal salt is interacted with hypophosphite at lower temperature 250 – 350 ^{o}C, it forms metal phosphine.Further interaction with sodium borohydride forms metal phosphide because it reduces metal ions to metal neutral. Even, H_2 plasma can produce very reactive H atoms, which can reduce metal ion to metal neutral.

2.3.4 Metathesis reaction

Metal halide can interact with Na_3P in inert atmosphere to form metal phosphide. Here, there is an exchange of ions between precursors.

2.4 Synthesis methods of borides

2.4.1 Solid state synthesis method

In solid state synthesis method, stoichiometric amount of metal (M) powder is mixed with amorphous boron (B) powder and then a mixture is heated at 500-600 ^{o}C to remove absorbed water, oxygen in vacuum or Ar-H_2. The pellet is prepared from this mixture, and then heated at 1000 ^{o}C or above in Ar atmosphere. Even, at different pressures, different phases of metal borides can be prepared.

A few examples are given. NbB or NbB_2 can be prepared by taking suitable stoichiometric amounts of Nb and B at 1000 ^{o}C in Ar atmosphere. At lower temperatures (say 700-800 ^{o}C), a mixture of Nb and $Nb_xB_y$is formed. At high temperature (1800 ^{o}C), phase of Nb_3B_4 is formed. Also, at high pressure of 4 GPa and high temperature of 1600 ^{o}C, the phase of NbB_2can be formed.
The phase MgB_2 can be prepared by heating a mixture of Mg and B powder (1:2 mole ratio and pressed into pellets) at 700 ^{o}C for 10 h under Ar atmosphere.

2.4.2 Electrolysis reaction method

Metal borides can be prepared using electrolysis method at higher temperature using molten salt or electrolyte. Three methods are provided here.(1) Metal borides are formed between B and M powder in LiCl/Li melt electrolyte at 900 ^{o}C.(2) Electrolysis of KBF_4 and metal salt can give metal borides. Metal salts are $FeCl_3$, $HfCl_3$.(3) Metal borides can be formed from metal salt electrolyte. Example. TiB_2 can be prepared from NaCl – KCl – NaF – K_2TiF_6 – KBF_4 system.

2.4.3 Reduction process under catalysis

Metal borides can be prepared at lower temperature in the presence of catalysts such as carbon (C) or aluminum (Al) or magnesium (Mg).

3.   Characterization of materials

XRD patterns of material can provide crystallinity of materials with structures. FTIR/Raman spectrum will provide their chemical bonding. Elemental composition of sample can be determined by chemical analysis techniques such as the Kjeldahl method, RBS, XPS, EDAX, etc. Morphology studies can be performed using SEM, TEM, HRTEM, AFM, MFM, etc.

4.   Properties of materials

Properties of materials can be studied using electron transport, magnetoresistance, magnetization, Hall effect, optical (absorption, luminescence), catalysis, harness, abrasive measurements.

5.   Conclusions

Many synthesis methods of binary compositions for nitrides, carbides, borides and phosphides are provided. Also, a few synthesis methods of ternary compositions will be covered. A few examples of materials with characterization techniques and their properties will be provided.

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Electro-valorization to synthesize value-added chemicals

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Executive Summary

Most chemical syntheses draw their raw materials from the current fossil fuel supply. Therefore, the research community should look beyond fossil fuels to establish sustainable chemical synthesis. Towards this end, several promising methods have emerged. Among them, the electro-organic synthesis (EOS) method and electro-activation (EA) of small molecules into value-added chemicals like lower hydrocarbons from CO_2 and NH_3 from nitrogen sources have attracted particular attention due to their environmentally benign and cost-effective nature. EOS is becoming popular due to its precise control, generating intermediates that are not accessible by conventional chemical routes and offering novel pathways in synthetic organic chemistry. In the literature, EOS is demonstrated for C-N functionalization, C-C coupling, C-H oxygenation, annulation, halogenation (**Scheme 1**), etc. By EOS, bio-based feedstocks can be used instead of fossil fuel, limiting carbon footprint. EA explores CO_2 sequestration and hydrogen storage in view of reducing carbon footprint. For example, electrochemical production of ammonia from various sources could be a low carbon footprint approach and alternative to the existing Haber-Bosch synthesis. In this talk, I will delve into the basics of electrochemistry to orient novices to foray into the EOS field. Besides, an account of the electro-syntheses performed and the electrochemical tools used in this field will be reviewed.
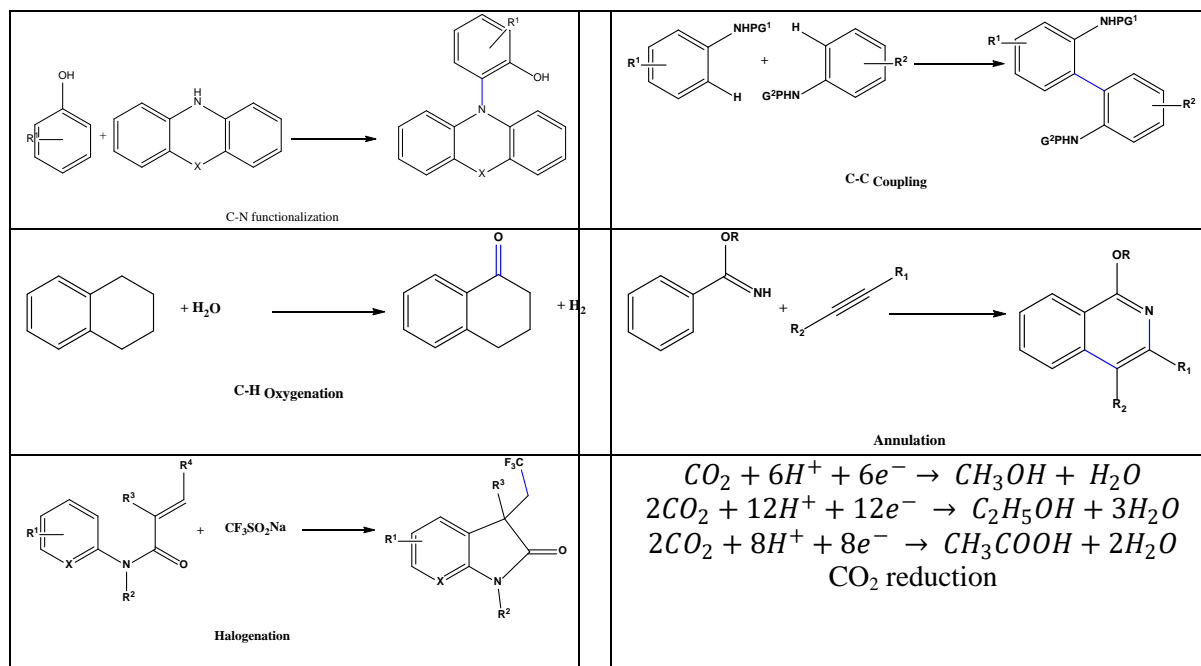
Basic requirements for EOS and Cell designs

In EOS, the electrodes play a vital role as the electro-organic conversions occur as heterogeneous chemical reactions at the interface of a solid electrode and a liquid electrolyte. The organic substrate is usually dissolved in the electrolyte.Besides, the electrolyte contains an (electro-) chemically inert solvent and supporting electrolyte to avoid leakage of current supplied for the side reactions, to generate high field strength across the double layer to initiate electron transfer and to maintain sufficient ionic conductivity in the bulk electrolyte. The supporting electrolyte could be either a salt, acid, or base. Generally, salts with inert ions that are profusely soluble in the solvents, like tetraalkylammonium hexafluorophosphate or tetrafluoroborate, are used as electrolytes. The most used electrodes are Pt, boron-doped-diamond, DUOCEL® RVC, SIGRADUR® glassy carbon, SIGRAFIL® carbon roving, SIGARAFINE® isostatic graphite. The Choice of carbon allotropes significantly affects the fate of the reaction and hence plays a vital role in selectivity, reactivity, and performance of the organic transformations. The potential (oftencalled voltage) applied across the working and counter electrode distinguishes EOS from regular chemical synthesis. In the laboratory, a three-electrode cell is generally used, wherein the third electrode is called a reference, concerning that potential is set at the working electrode using an electrochemical workstation.

The electrochemical workstation pushes the electrons into the cathode, pulling them out of the anode. When the electron flows through the external circuit, equivalent ionic current flows through the reaction medium, i.e., electrolyte. An electrochemical workstation works as a power source, either in a galvanostatic or potentiostatic mode. The current supplied is fixed in galvanostatic mode, letting the applied potential vary. In the potentiostatic mode, the applied potential is fixed (usually in three-electrode mode), letting the current flowing between the working and counter electrode vary. For the reaction to occur, the substrate should reach the electrode-electrolyte interface by a suitable mass transport to undergo a redox reaction (electron transfer). After which, the product formed must move away from the interface, paving the way for further reaction. Therefore, it is essential for both the substrate and product to remain soluble in the electrolyte with sufficient diffusion coefficient to

achieve decent current density and, hence, the production rate. This electron transfer is termed electrolysis, as energy is usually input to carry out EOS. Electrolysis is of two types, namely direct and mediated. In direct electrolysis, a heterogeneous electron transfer reaction happens, whereas, in mediated electrolysis, an electroactive mediator is used to carry out homogeneous electron transfer with the substrate dissolved in the electrolyte. In some cases, subsequent to interacting with the electrode, the electroactive mediator is pumped out of the cellto conduct a homogeneous reaction with the substrate in another vessel.

The cells commonly used are divided, undivided, and quasi-divided type. In quasi-divided cell, the features of divided and undivided cells are hybridized. Usually, it constitutes electrodes of two different surface areas, and they are exposed to different environments.

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$
$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$$
$$2CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH + 2H_2O$$
CO$_2$ reduction

Scheme 1. EOS reported in the literature involving C-N functionalization, C-C coupling, C-H oxygenation, Annulation, Halogenation, and EA of converting CO$_2$ into value-added organic chemicals.

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Synthesis of Low Dimensional Materials:
A tale of different Synthetic Techniques

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Introduction

Particles ranging in size from roughly 1 to 50 nm exhibit physical and chemical properties that are intermediate between those of the smallest element from which they can be composed (such as a metal atom, the stoichiometric unit of a metal oxide) and those of the bulk material. Owing to their nanoscale dimensions with possible quantum limit, nanomaterials and nanostructures possess a high surface-to-volume ratio, rich surface/interface effects, and distinct physical and chemical properties compared with their bulk counterparts, leading to the remarkably expanded horizons of their applications. Depending on their degree of spatial quantization, low-dimensional nanomaterials are generally categorized into nanoparticles (0D); nano-rods, nanowires, and nano-belts (1D); and atomically thin layered materials (2D).Some examples include nano-flowers, nano-cubes, nano-cages, nanowire bundles, as well as other self-assemblies of lower dimensional nanomaterials. A typical methodology towards nanostructured material fabrication can be classified into two broad categories, i.e., (i) ***Top-down approach*** and (ii) ***Bottom-up approach***. In the top-down approach, one starts with bulk material (in orders of microscale), then breaks this bulk material using numerous techniques to form a nanoscale particle/structure, whereas in the case of bottom-up approach one starts with smallest scale possible then makes its way up the dimensions till nanoscale particle/structures are achieved.Many methods in these approaches are well-suited to current industry technology.

Top-down approach basically revolves around removing a part of material from the starting bulk solid to achieve fabrication in orders of nano/micro scale which in layman's language, we can think of the top-down fabrication approach as a process similar to thatof a sculpture artist's process of sculpting a sculpture from a block of stone. The top-down approach is comparatively simpler as the process involved depends either on the removal or break down of bulk material or on miniaturizing the existing bulk fabrication protocol to produce the desired micro/nano structure with appropriate size, chemical, and physical properties Fabrication over a large substrate is possible and reliable. Yet, it could come with the price of imperfections induced on surface structures. Traditionally top-down techniques used for creating nanostructures and nanopatterns are: a) Lithography & different Lithographic techniques: viz. –(Photolithography; Ion Beam Lithography; Scanning Probe Lithography; Nanoimprint Lithography; Contact Lithography, Electron Beam Lithography) *etc.*; b) Ball milling; c) Sol-Gel Method; d) Template Etching.

Contrary to the top-down approach, the bottom-up approach uses chemical and mechanical forces operating at nano/microscale to assemble the basic units into larger structures. Motivation for bottom-up approaches comes from systems guided by nature, where nature utilizes various chemical forces to fabricate/produce essentially all the edifices needed by life. Researchers always try to replicate/simulate nature's ability to produce nano/micro clusters of specific elements, which can then self-assemble as one to form. The different process that has been followed for the bottoms up techniques are: a) Plasma Arching; b) Chemical Vapour Deposition (CVD); c) Atomic Layer Deposition (ALD);d) Pulsed Laser Deposition (PLD); e) Laser Pyrolysis; f) Molecular Beam Epitaxy (MBE); f) Molecular Self-Assembly (MSA).

Originating from the fields of physics, chemistry, materials science, and chemical engineering, this area of study is now often referred to as nanoscience. The term "nano" means dwarf and nanotechnology can be understood as the multidisciplinary science of developing, characterizing, and synthesizing materials by controlling their sizes and shapes at the scale of nano-meters and sub nanometres. With the reduction of particle size, coordination unsaturated metal species increase

obviously and benefiting from their low-coordination and unsaturated configuration, single atom catalysts have been more catalytically active than even nanometer-sized metal particles.

2. Characterization of Low Dimensional Materials

Material characterization methods for detecting the so called mystery of the low dimensional materials are very strongly developed. Though initially proposed and described long time ago by the related basic theories microcosmic defects in materials have been clearly recognized. Strong research of solid defect chemistry also had a large development from the initial theoretical prediction and macro measurement to the characterization and understanding of microscale. In order to study the effect of defects on catalysts, it is necessary to identify the defect structure at first. As seeing is the believing, the correlation of the structural defect sites in the nano dimensional materials and catalytic activity could only be perceived to the best extent by proper characterization and quantification of the defect sites and then understanding their effect over the catalysis. Presently the Characterization methods can be broadly divided into two methods mainly: a) **Microscopic Characterization Methods**; b) **Spectroscopic Characterization Methods; c) Diffraction and Topography.** Although determination of the type, population and distribution of defects can be a critical and may not be possible by a single technique, yet each technique that is applied has specific limitations and certain positive points. Certain microscopic and spectroscopic techniques for determining effect of particle size on catalysis are enumerated here.

A. Microscopic Techniques:
1) High Resolution-Transmission electron microscopy (HRTEM/TEM)
2) Aberration corrected transmission electron microscopy (ACTEM)
3) Scanning Transmission Electron Microscopy (STEM)
4) Atomic force microscopy (AFM)/Kelvin probe force microscopy (KPFM)
5) Scanning tunneling microscopy (STM)
6) Scanning Electron Microscopy (SEM)

B. Different Spectroscopic Techniques
1) X-Ray photoelectron spectroscopy (XPS) and Auger Electron Spectroscopy.
2) X-Ray absorption spectroscopy (XAS)
3) Electron paramagnetic resonance spectroscopy (EPR)
4) Solid State -NMR
5) In situ FT-IR

At this microscopic level, some characteristics of a single atom are significantly different from those of the sub-nanometer clusters or nanometer particles, thereby rendering SACs to possess extraordinary catalytic selectivity, activity, and stability, including (i) unsaturated coordination configuration of catalytic centres, which produces active sites that are accessible to reactant; (ii) quantum size effects, in which electrons confinement leads to a distinctive HOMO–LUMO gap and a discrete energy level distribution; (iii) strong metal–support interactions, which guarantee charge transfer between metal and associated interface; (iv) foreign atom effect, which would produce asymmetrical spin and charge density. All these characters make SACs different from those bulk nanoparticles

Synthesis Strategies for Low Dimensional Catalytic Materials

Historically going the majority of methods involve the creation of metal particles on a pre-formed support. There is, important route which is used specially for nickel/ silica and nickel/ alumina and which involves *co-precipitation* of the precursors (typically the hydroxides) from homogeneous solution, followed by washing, drying, calcination and reduction, during which the final desired characteristics of the catalyst are developed. The *vapour phase methods (CVD & PVD)* were performed in the absence of other components save the residual gas, and it is metal atoms or clusters thereof which arrive at the surface. This is not of course true if carbonyl complexes are the vehicle by

which the metal is brought to the surface. When *colloidal dispersions* are formed and caused to adhere to the support, their size and structure is again not influenced by the support, but the liquid medium can contain species which are by-products of the preparation and which may obscure the situation unless removed by dialysis. In the second group of methods, the metal, the metal particles nucleate and grow at the support surface and these processes are thus under the influence of its physical and chemical identity. In the case of *vapour deposition,* metal atoms condense on the support surface, forming either continuous monolayers (Frank-Van der Merwe growth) or discontinuous three-dimensional particles (Volmer-Weber growth) or a monolayer succeeded by particle growth at isolated sites (Stranslc-Krastanov growth). That which obtains is determined by the relative interaction energies between metal-metal and metal-support atoms to diffuse and agglomerate, and thus the stabilization of isolated atoms is of vital importance in the processes of catalyst design and construction.

Fabrication of single atom catalysts (SACs), however, has been challenging as the tendency for aggregation of metal atoms either during the synthesis processes or the subsequent treatments. During the past decade, several approaches to construct isolated metal sites over catalyst supports have been reported, including (i) lowering the loading amount of metal components; (ii) enhancing the metal–support interactions; (iii) utilizing vacancy defects on supports or voids in supports. All proposed strategies are aiming at preventing isolated atoms from aggregation and/or strengthening the metal–support interactions. In most instances, the support for singly distributed catalysts is deliberately selected. Certain strategies are tabulated below.

Sl. No.	Synthesis Strategy	Support	Catalyst	Catalytic Application	References
1.	Wet-impregnation method	FeO_x	Pt	CO oxidation	1
2.	Atomic layer deposition	Graphene	Pt	MeOH oxidation	2
3	Photochemical route	TiO_2	Pd	Hydrogenation of Benzaldehyde	3
4	High temperature atom trapping	Graphene	Nb	Cathodic oxygen reduction reaction	4
5	MOCs derived	Graphene	Fe	Catalytic benzene oxidation	5
6	Modular synthetic approach	MOF	Co	Photocatalytic CO_2 reduction	6

Table-1: Synthetic Approaches for synthesis of Single Atoms on surfaces to be used as single atom catalysts.

4. Conclusions and future directions

The different synthetic techniques discussed above leads to differential bond strength, bond length in the specified nanoclusters and sub nano clusters. These heteroatomic bonds can be polar and result in substantial charge transfer from either active metal to the support, or electron- deficient sites present over the metals as created by the synthetic mechanism. These leads to a variety of change in the different properties in the molecular level as the defects, and electron density are majorly guided by the specific synthetic methodology. Therefore, in order to achieve a particular property, it becomes essential to synthesize in the proper way as being isolated from each other, the atoms once anchored to a support through a variety of interactions. Tuning these interactions becomes requisite way to engineer single atom surfaces intended for specific catalytic applications.

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He is the recipient of DAE Young Scientist Award-2012. He was awarded the Young Research Associate-MAS-2017. He has more than 72 publications in the journals of international repute like ACS Catalysis, ACS AEM, JPC, RSC, Chem Euro, *etc.,* and is in the reviewer's panel of several of several International Journal of repute like JPC, JSST, JALCOM, Langmuir, IJHE, *etc.* His has guided 2 PhD students and presently 2 PhD students are working under him several project trainees and one Inspire Faculty Fellow. He is working on the field of Catalysis and Hydrogen Energy presently in BARC and is an Associate Professor in the Homi Bhabha National Institute.

"AI/ML Based Design and Synthesis of Materials"
Guiding Experiments through Quantum Chemical GPS

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Abstract

Designing a catalyst for given reaction is a challenging task. An, important aspect in the active catalytic species involving transition metal ions are intermediates whose life-times are typically shortand unstable at room temperatures. X-ray crystal structures are often difficult and thus spectroscopic techniques are the only way to characterize these short-lived intermediates. Artificial Intelligence/Machine Learning (AI/ML) methods are still at its infancy for the design of active catalyst at room temperature. To complicate things further, the spectroscopic parameters of these transient molecules are reliable; their corresponding interpretations may be misleading and thus special care should be taken towards analysing the data. In this talk, I will show-case the importance of electronic structure calculations to characterize these short-lived intermediates with some examples. In addition, based on modelling techniques, we propose new experiments that can be synthesized in the laboratories in the field of supramolecular catalysis. We firmly believe that computational chemistry predictions can be used to guide new experiments.

High performance computing hardware has become cheap, efficient and user friendly quantum chemical reaction modeling is common even in the experimental community. Commercial molecular modeling software is attractive to pursue high-quality research. In particular, the dawn of density functional theory (DFT) as a *de facto* standard in reaction modeling opened the door to obtaining useful and realistic models of complicated chemical reactions.[1-3]Initially, computer models were employed to rationalize and better understand and support experimental observations, often using minimalistic models to keep the computational cost tractable.Presently, molecules of realistic size and complexity can now be calculated and complete reaction cycles can now be modeled with little to no structural simplifications.

One particular research area that has been focused is the design of suitable catalyst involving transition metal ions. The next logical step is employing these models to optimize, if not predict, new reactions beyond what purely experimental approaches allow. There are several obvious potential advantages of virtually optimizing novel or practical catalysts and developing new reactions in the computer before experiment.[4] Once a mechanism is established with a computational model, making changes to the catalyst and substrate compositions to assess the impact of such changes is relatively easy and can require little time and effort, compared to experiment. Virtual screening efforts with the aim of discovering molecules and material with desirable properties are rapidly gaining popularity.Due to the complexity of reaction mechanisms; these reactions often require special attention. While automated optimization techniques have seen remarkable advances, most successful studies still rely on classical chemical logic and conventional strategies of reaction design. In addition to delivering energies and structures of intermediates that may not be accessible experimentally, DFT calculations offer the unique advantage of allowing for a qualitative examination of the electronic structure that is responsible for the numerical result in question.[5] In principle, general concepts that not only explain one specific reaction but are valid for a whole class of reactions can be obtained from a detailed analysis of the computed results.

Catalysts for Small Molecule Activation

Small molecules are often inert due to their very large bond dissociation energies that range from ∼100 to ∼260 kcal mol^{-1}as shown in table 1.[6] When these molecules are activated, they can be converted to commodity chemicals such as methanol (from CO_2) or ammonia (from N_2). Additionally, due to the serious environmental problems, the chemical conversions represent an avenue of green environment.

Table 1. Bond dissociation energies (units in kcal mol^{-1}) of some molecules.

Molecule	ΔE	Molecule	ΔE
H_2	104.2	CO_2	128.4
N_2	228.6	H_2O	118.8
O_2	120.3	NO	152.8
CO	258.9	CH_4	103.5

Many of these reactions are successfully carried out in nature by metalloenzymes sometimes involving multi-metallic active sites as found in photosystem II (H_2O oxidation), nitrogenase (N_2 fixation), and hydrogenases(H_2 splitting), to name a few prominent examples. In almost all cases, these activations are redox reactions and the necessary protons and electrons are often provided by amino acids and electron transfer proteins. Inspired by these enzymatic systems, both experimental and computational studies have been carried out to understand the mode of action and possibly to engineer artificial systems that can carry out the same reactions. Small molecule activation in general is a large research area with a long tradition.

With the rapid development of software and hardware technologies to make computational modeling tools more reliable, they can now provide valuable insights and even become predictive. We need to collect more spectroscopic and structural data such that the structure-function relationship of the catalyst can be designed through AI/ML based techniques.

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Synthesis strategies for smart polymeric materials

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Nature has always inspired and fascinated us through the smart behaviour of various materials like the leaves of *Mimosa Pudica*, Venus flytraps, the photosensitivity of sunflowers and the colour sensitivity of chameleons. Materials that can understand the surrounding materials and react precisely to it are called smart materials. Polymeric materials which can behave smartly to such environmental stimuli have opened new areas of research in biomedical engineering for cell culture, drug delivery and therapeutics, personal health care and hygiene products, agriculture, waste water treatment, sensors and actuators, textiles, and flocculation. The external stimuli for smart responsive materials can be physical, chemical or biological. [1]

The characteristics of different polymers is based on how the long chains of the molecules repeat themselves and bond with each other. The inherent structure, along with the way molecules arrange themselves and cross-link, aids materials' responsiveness to trivial environmental changes. To understand the method by which these materials are synthesized, a basic knowledge of polymerization is required. There are some principles which are common to a wide variety of preparation methods. This will be the main focus of this talk.

The following polymerization methods will be covered:

1) Anionic chain polymerization
2) Radical chain polymerization
3) Cationic and metal catalyzed chain polymerization
4) Chain copolymerization
5) Ring opening polymerization
6) Step polymerization
7) Post polymerization functionalization

Among the smart polymers, hydrogels are the most widely used and well known. The mechanism of stimuli-response, such as volume change, phase transition, or structural change, points to the gelator-gelator and gelator-solvent interactions. The formationof hydrogels involves three steps. First, hydrophilic groups of gelators were hydrated by water molecules to form the primary bound water, and then water molecules came to the exposed hydrophobic groups forming the secondary bound water. Third, the osmotic force from gelators drew a large amount of water molecules cominginside the network and drove the whole system to dissolution, however, resisted by crosslinks. The system finally came to a balance to form a hydrogel. Thus, the gelator-gelator and gelator-solvent interactions play a key role in design and regulation of stimuli-responsive hydrogels.[2]This part of the talk will briefly cover the classifications of hydrogels based on the stimuli responsiveness and subsequently, typical polymerization techniques for hydrogel synthesis will be introduced. The following polymerization techniques for synthesizing stimuli responsive hydrogels will be covered in detail:

Chain growth polymerization

Chain growth polymerization employing a free radical mechanism is a popular strategy to synthesize chemically crosslinked hydrogels. The polymerization process involves three steps: initiation, propagation, and termination. The steps and mechanism of polymerization will be discussed.

Bulk polymerization

Bulk polymerization is widely applied to produce hydrogels because of its simple mechanism. This technique involves the polymerization of liquid monomers and monomer soluble einitiators with a small amount (<5%)of crosslinker. The polymerization process is typically initiated using ultraviolet light, radiation, and/or chemical catalysts. Few examples of stimuli responsive hydrogels formed by bulk polymerization and the parameters to be taken care of will be discussed.

Solution polymerization

In solution polymerization,ionic or neutral monomers with a solvent (e.g., benzyl alcohol,water, ethanol, or water–ethanol mixtures) and multifunctional cross-linkers undergo polymerization by ultraviolet (UV) or redox initiation to form hydrogels. Solution polymerization is well-known for ease of synthesis and low-cost processing with better heat transferand control during polymerization.

Suspension polymerization (including inverse-suspension polymerization)

Suspension polymerization generally involves insoluble monomers and initiators with a low hydrophilic–lipophilic balance suspending agent in aqueous solution. They are constantly agitated to create droplets of monomers(0.1–5 mm in diameter). As polymerization proceeds, the polymer hydrogel beads are formed, which can be filtered to separate from the reaction mixture. The process parameters used in the protocol will be discussed with few examples.

Emulsion polymerization (including micellar polymerization)

Synthesis of hydrogels can also be done by emulsion polymerization. A typical emulsion polymerization process involves a water-soluble initiator, a surfactant, crosslinker, and monomers which are slightly water-soluble or completely hydrophobic. In inverse emulsion polymerization, a hydrophilic monomer dispersed in an organic phase is used.

Graft polymerization mechanism.

Polymers with poor mechanical properties can be grafted onto more robust support frames.[3,4]In this process usually, free radical sites are generated on the surface of the support where monomers can be directly polymerized to form stronger covalent bonds with the support structure.

Step-growth polymerization

Step-growth polymerization utilizes distinct functional groups containing monomers to synthesize hydrogels. These complementary functional groups react and form covalent bonds to propagate a one-step polymerization process.

Conclusion

These topics are those which give basic understanding of the principles and conditions used for synthesizing smart polymeric materials. Some of the synthesis strategies are not discussed here not due to lack of relevance or importance. The knowledge of these polymerization methods will help young people working in this area to design their own materials. Further, state-of-the-art techniques used for hydrogel characterization and their importance will be highlighted under each synthetic strategy.

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Molecular precursor mediated synthesis of nano-sized materials

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Abstract

Nanomaterials have emerged as a pivotal class of materials, revolutionizing modern science and technology. They are instrumental in various energy devices, propelling efficiency and efficacy. Beyond energy applications, nanomaterials are integral in addressing global challenges in healthcare and the environment. The synthesis of nanomaterials is a crucial aspect, with soft chemical routes playing vital roles. The single-source molecular precursor (SSP) method, belonging to the metal-organic/organometallic class, offers a promising avenue for creating well-defined nanostructures. It provides precise control over composition, morphology, and particle size, fostering interest as an effective design method. This article explores SSPs, their advantages, and their applications in producing diverse nanostructures, encompassing metal oxides, metal phosphides, and metal chalcogenides, offering a glimpse into the future of tailored nanomaterials.

Introduction

In the realm of modern science and technology, nanomaterials have undeniably emerged as a captivating class of materials, drawing immense interest and demand across a broad spectrum of practical applications. Their unique characteristics and versatility have propelled them to the forefront of numerous cutting-edge technologies, reshaping the landscape of various industries. Nanostructured materials, with their dimensions falling within the remarkable range of 1 to 100 nanometers in at least one dimension, have become the focal point of research and development in a multitude of energy devices which has benefitted significantly from the integration of these nanostructured materials, revolutionizing their efficiency and efficacy. The influence of nanomaterials transcends the realm of energy applications. They are rapidly becoming pivotal in environmental and healthcare sectors, showcasing their potential to address pressing global challenges.

The marvel of nanotechnology lies in its ability to engineer these nanomaterials, presenting a pathway to substantially improve the performance of various products. Beyond the quantum confinement effect which stems from the nanoscale dimensions, a multitude of physical and chemical properties, such as magnetism, optical attributes, and catalytic activity, exhibit a strong dependence on composition, shape, and size, underscoring the importance of the synthesis method. The method of synthesis plays a pivotal role in shaping the properties of nanomaterials, directly impacting their potential and versatility in nanotechnology applications.

Over time, several innovative strategies have been developed to arrive at nanostructures with specific physico-chemical characteristics. These synthetic strategies can be broadly classified into top-down and bottom-up approaches. The top-down approach in nanomaterial synthesis involves the reduction of bulk materials into nano-sized entities through various methods such as milling, lithography, and etching. One of the primary advantages of this approach is its ability to create nanostructures with a high degree of precision and control. However, this approach has its limitations. It is energy and resource-intensive, potentially leading to materials with defects or altered intrinsic properties. Moreover, the process can generate a considerable amount of waste, raising valid environmental concerns. On the other end of the spectrum are high-temperature solid state methods including pyrolysis, microwave-assisted synthesis, calcinations, combustion, etc. However, most of these processes often lead to impurity phase formation or extensive agglomeration compromising the surface area of the nanostructures and exert poor control over the morphology, composition, as well as chemical and electronic properties of the materials, leading to poor activities.

Beyond these methods, there are more refined approaches to produce well-controlled and efficient materials through various solution-phase methodologies. These encompass solvothermal/hydrothermal, ultrasonication, co-precipitation, heat-up, and hot injection methods. Moreover, nanomaterials can be deposited as thin films using chemical vapor deposition (CVD) techniques, including metal organic-CVD (MOCVD), low pressure-CVD (LPCVD), liquid injection CVD, aerosol-assisted CVD (AACVD), and solution processing techniques to develop nano-ink and chemical bath depositions. These synthetic strategies mainly align into two categories based on the nature and type of precursor used: single-source molecular precursor method (SSP) and dual/multi-source precursor method.

Single Source *vs* Dual/Multi Source Precursor Route

The dual/multi-source route involves the utilization of distinct organic/inorganic molecules or salts for each constituent, often characterized by toxicity and sensitivity to air and moisture. In contrast, the single-source molecular precursor (SSP) method employs a precursor typically belonging to the metal-organic/organometallic class, where the desired constituents are present in the molecule with a direct covalent bond between them or, rarely, in an unbounded state. This approach offers notable advantages for material synthesis, ensuring well-defined stoichiometry and homogeneity compared to multi-source approaches. It promotes the formation of nanosized particles with high surface areas and reduces the required crystallization temperature for material synthesis, typically resulting in the formation of pure phases (Figure 1). Overall, the SSP route provides the advantage of precisely tailoring the structure, morphology, and particle size at relatively mild temperatures. It enables the design of materials on an atomic scale, achieving compositions that would otherwise be inaccessible via traditional methods, thus heightening interest in recent years as a favorable design method [1, 2].

Among solvent-mediated strategies, hot-injection and heat-up routes, and among solvent-less strategies, solid-state pyrolysis, stand out as particularly appropriate for the utilization of single-source molecular precursors (SSPs). Furthermore, SSPs demonstrate excellent suitability for synthesizing thin films using the chemical vapor deposition (CVD) route. The synergy between SSPs and these mentioned strategies has proved highly successful in the production of diverse nanostructures, encompassing metal oxides, mixed metal oxides, semiconducting metal chalcogenides, metal phosphides, metal alloys, and composites. This amalgamation of techniques has widened the horizons for the controlled and precise synthesis of nanostructures, enabling the development of advanced materials with tailored properties and applications across various domains.
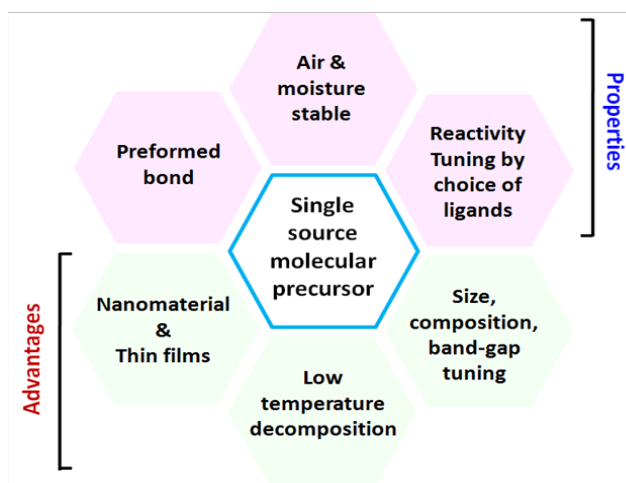
Figure 1. Schematic representation of important advantages associated with single source molecular precursors.

Selecting Suitable SSP

Selecting an appropriate Single-Source Molecular Precursor (SSP) is a crucial step in the design and synthesis of various classes of nanomaterials and thin films. The ligand system plays a vital role in determining the structural stability and chemical reactivity of the precursor. Therefore, choosing the right ligand system is a critical aspect when considering a suitable SSP. Recently, a special class of ligands known as internally functionalized hemilabile ligands has gained significant

attention. These ligands encompass both soft/intermediate and hard donor sites within the same moiety, enabling reversible coordination with the metal ion. This feature ensures compatibility with a wide range of metal atoms, regardless of their hardness or softness. Ensuring the purity of the SSP is equally important. The SSP should be easily separable from the reaction media, either through recrystallization or solvent extraction, with minimal impurities or by-products. Additionally, the SSP should be non-toxic and possess an adequate shelf life under ambient conditions, exhibiting stability in the presence of air and moisture. These considerations serve as essential guidelines when selecting an SSP for the preparation of nanomaterials.

From SSP to Materials

The conversion of the molecular precursor into a material involves a structural rearrangement and the removal of organic ligands (Scheme 1). The innovation lies in reducing the activation barrier for solid-phase nucleation through the preformed metal-ligand bonds (e.g., M−E; E can be N, P, O, S, Se, Te) present in the molecular precursor, thus markedly lowering the operation temperature [3]. In the subsequent section, specific examples pertaining to Single-Source Molecular Precursors (SSPs) for metal oxide, metal phosphide, and metal chalcogenides will be discussed.

$$ME_n \; + \; L \; + \; L'$$

$$ME_nLL'$$
$$(SSP)$$

$$ME_{n-m} \; + \; mB \; + \; L \; + \; L'$$
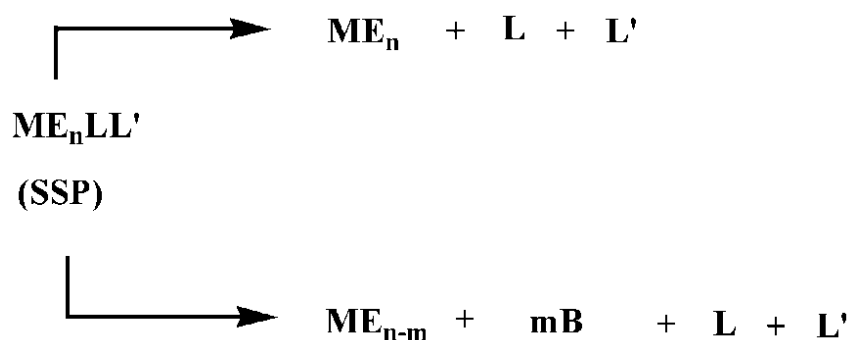
Scheme 1. Two possible modes of action of single source molecular precursors.

SSP for metal phosphides

Metal phosphides have emerged as highly promising materials for catalytic upgrading processes of bio-oils, offering a potential avenue for renewable and cost-effective liquid fuel production. Single-Source Molecular Precursors (SSPs) derived from phosphine and its derivatives provide an efficient pathway for generating high-quality metal phosphide nanomaterials [4]. Additionally, complexes adorned with bridging-diphenylphosphide, diselenodiphosphate, and similar motifs offer appealing alternatives for the synthesis of metal phosphides, broadening the spectrum of viable synthetic routes in this domain.

SSP for metal oxides

Metal oxides find extensive and diverse applications in various fields, including solar cells, photocatalysts, batteries, transistors, supercapacitors, superconductors, luminescent materials, and gas sensors. Within the realm of Single-Source Molecular Precursors (SSPs), metal alkoxides prove to be excellent candidates for generating monodisperse metal-oxide nanoparticles at relatively low temperatures. The bulky alkoxide ligands surrounding the metal centers play a crucial role in preventing the agglomeration of the final metal oxide nanomaterials. Additionally, research has shown that ternary metal oxides, such as the multifunctional BaTiO3, can be readily produced using mixed metal alkoxide-hydroxide complexes. This approach allows for high compositional purity, low crystallization temperatures, and nano-dimensions with low dispersity, further expanding the potential applications of metal oxides [5].

SSP for metal chalcogenides

Two-dimensional atomically thin semiconductor nanostructures, such as tin monochalcogenides (SnE, where E = S, Sn) and tin dichalcogenides (SnE$_2$, where E = S, Se), have garnered significant global attention owing to their remarkable electrical and optical properties. Various complexes derived from different classes of ligands, including xanthates, thiolates, chalcogenoether, and chalcogenolates, have been investigated for the fabrication of high-quality metal chalcogenide nanostructures. Recently, ligands with internal functionalization, featuring soft chalcogen and hard nitrogen atoms, have emerged as highly sought-after for creating Single-Source Molecular Precursors (SSPs). These SSPs can undergo facile conversion into nanomaterials and thin films of metal chalcogenides under relatively mild conditions, further enhancing their appeal in nanomaterial synthesis [6].

Conclusion

To summarize, this article has explored the significant strides made in recent decades regarding Single-Source Molecular Precursors (SSPs) for technologically relevant materials, including metal oxides, phosphides, and chalcogenides in the nano-regime. SSPs present a multitude of unique advantages over the multi-precursor approach, showcasing improved phase purity, reproducibility, lower activation barriers for nanostructure formation due to preformed bonds, and applicability in crafting nanomaterials and thin films. The judicious selection of a ligand system in SSP design is paramount, given the diverse coordination behaviors and atom transfer abilities of ligands. Some ligands encourage chelation, while others facilitate oligomerization. Moreover, varying ligand systems possess distinct metal-coordinating atom bond strengths, offering ample opportunities to fine-tune the composition and properties of the resulting materials. The embrace of SSPs represents a promising avenue to tailor nanomaterials, meeting the evolving technological landscape's demands.

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