**Special Issue on**

**"Role of metal chalcogenides in energy conversion and storage"**



## SOCIETY FOR MATERIALS CHEMISTRY

# Society for Materials Chemistry

Society for Materials Chemistry was mooted in 2007 with following aims and objectives:

(a) to help the advancement, dissemination and application of the knowledge in the field of materials chemistry,

(b) to promote active interaction among all material scientists, bodies, institutions and industries interested in achieving the advancement, dissemination and application of the knowledge of materials chemistry,

(c) to disseminate information in the field of materials chemistry by publication of bulletins, reports, newsletters, journals.

(d) to provide a common platform to young researchers and active scientists by arranging seminars, lectures, workshops, conferences on current research topics in the area of materials chemistry,

(e) to provide financial and other assistance to needy deserving researchers for participation to present their work in symposia, conference, etc.

(f) to provide an incentive by way of cash awards to researchers for best thesis, best paper published in journal/national/international conferences for the advancement of materials chemistry,

(g) to undertake and execute all other acts as mentioned in the constitution of SMC.

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Contact address
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C/o Chemistry Division
Bhabha Atomic Research Centre, Trombay, Mumbai, 400 085, India
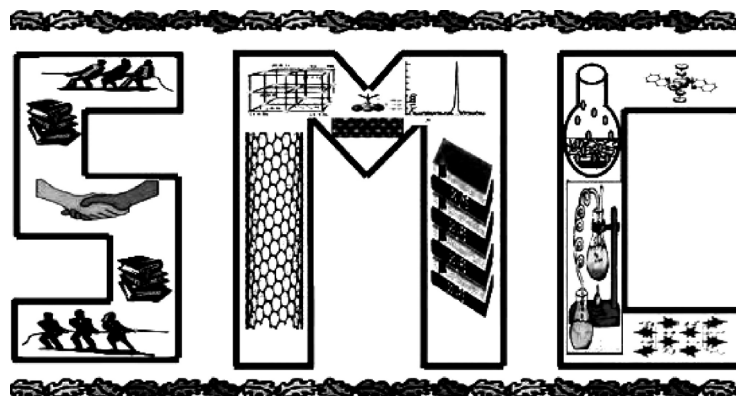Tel: +91-22-25592001, E-mail: socmatchem@gmail.com

Special Issue on

# Role of metal chalcogenides in energy conversion and storage

**SOCIETY FOR MATERIALS CHEMISTRY**

# SMC Bulletin

# *Guest Editorial*



Dr. Adish Tyagi

Humanity finds itself at a pivotal crossroads, grappling with the ominous depletion of fossil fuels. This crisis not only jeopardizes our energy security but also exacerbates environmental degradation. Consequently, energy-related predicaments have taken centre stage in the global academic arena. In recent years, the pursuit of clean and sustainable energy solutions has garnered unparalleled attention. Within this context, nanostructured metal chalcogenides (MCs) have emerged as highly versatile and promising materials, holding tremendous potential for energy conversion and storage technologies.

The escalating interest in research on metal chalcogenides underscores not only their scientific significance but also highlights their profound economic and technological implications. This special issue of SMC serves as a compendium, offering a profound exploration of the pivotal role that metal chalcogenides play in energy conversion and storage materials. Dr. Kedarnath's insightful article acts as a brilliant introduction, showcasing the diverse ways in which metal chalcogenides can be harnessed for energy applications. Following this, Dr. Mandal's contribution delves into the potential of metal chalcogenides as anode materials for Lithium-Ion Battery (LIB) applications. In a complementary vein, Dr. Nigam's article intricately explores the structure, electronic properties of hosts, and ion movement channels of chalcogenides, all pivotal factors contributing to their enhanced electrochemical performance. Dr. Bhattacharya, a distinguished researcher in thermoelectric devices, presents an outstanding article on the potential of chalcogenides as the next-generation thermoelectric material. Concluding this compilation is an article by Dr. karmakar that sheds light on the common synthetic strategies employed to fabricate these intricate materials..

I am deeply honoured to serve as the guest editor for this special issue, titled "Role of Metal Chalcogenides in Energy Conversion and Storage." I extend my heartfelt gratitude to Dr. A. K. Tyagi, President of SMC, and the entire executive committee for entrusting me with this responsibility. I would also like to express my sincere appreciation to all the authors who responded promptly by contributing their articles. Special thanks are due to Dr. Gourab Karmakar for his valuable contribution to the cover page artwork. I hope the readers find the articles engaging and informative.

# From the desks of the President and Secretary



**Dr. A. K. Tyagi**



**Dr. Sandeep Nigam**

Dear SMC Members, Colleagues and Readers,

Warm greetings from the Executive Council of the Society for Materials Chemistry (SMC)!

There has been continuous effort of our editorial team to bring out contemporary thematic issues. The multidisciplinary nature of these issues makes them relevant to the researchers of different scientific background. In the same direction, current issue entitled "Role of Metal Chalcogenides in Energy Conversion and Storage" is another marching step.

As the title express, this thematic issue deal with application of Metal Chalcogenides for energy applications. First article introduces the Metal Chalcogenides and their uses to readers. The implication of metal chalcogenides for Lithium-Ion Battery (LIB) applications has been discussed in the subsequent two chapters. Another dimension of metal chalcogenide application i.e. thermoelectric has been narrated brilliantly in one of the article. The thematic collection also has an article describing the synthesis strategies.

We gratefully acknowledge Dr. Adish Tyagi who agreed to be the guest editor of this issue and put in efforts to bring out this special issue. We also acknowledge the efforts of all the contributing authors for submitting their informative articles. We also thank all the members of SMC for their continued support and cooperation in the growth of the Society for Materials Chemistry.

# CONTENTS

# Applications of Metal Chalcogenides for Energy Conversion and Storage Applications

**G. Kedarnath**
*Chemistry Division, Bhabha Atomic Research Centre, Mumbai-400 085.*
*Homi Bhabha National Institute, Anushaktinagar, Mumbai-400 094*
*Email: kedar@barc.gov.in*

## Introduction

Energy and environment pertaining problems are the most pivotal topics around which the twenty first century is swirling. Snowballing demand of the former combined with dwindling fossil fuel reserves can bring out severe impact on the global economy which in turn affect the livelihoods of the people. Therefore, cost-effective, efficient, and environmentally friendly sustainable renewable energy technologies are the need of the hour. To meet these requirements, development of energy conversion and storage devices such as solar cells [1-4], electrochemical water splitting cells [5,6], thermoelectric devices [7,8], batteries [9] and supercapacitors [10] is inevitable. The performance of these devices mainly banks on the device structure and active material. On both these fronts, lot of studies were envisaged and implemented. Yet, the breakthrough performance in many of these devices relies on nano structurization of the active materials. Of these, nanostructured metal chalcogenides have drawn substantial attention as an active material in these devices by virtue of their considerable abundance, absorption coefficient and carrier mobility. Further, the applicability of these metal chalcogenides is widened by the development of synthesis protocols for a broad range of sizes and shapes leading to exotic physiochemical properties. Additionally, miniaturization of the materials provides larger surface to volume ratio relative to their bulk materials, is advantageous for the devices not only due to the increased interaction among the particles but also due to interaction between the devices [11]. Therefore, quite a few articles [12,13] have reviewed the synthesis of metal chalcogenide nanostructures and their applications in various fields. The present article presents metal chalcogenide applicability in energy-conversion and -storage.

## Metal Chalcogenides for Energy Conversion

On the back drop of energy and environmental problems, clean and green sustainable energy resources including wind, solar, geothermal, tidal and biomass resources are being tapped globally. Yet, efficient utilization of these renewable energies is restricted by their large-scale storage requirement. These issues can be resolved by converting one form of the energy to other forms which can be stored conveniently.

In this framework, the conversion and storage of energy sources has been in the focus over a long time. Of these, conversion of solar energy to hydrogen via water splitting and utilization of waste heat for the generation of electricity through thermoelectric materials have drawn significant attention.

## Water Splitting

Electrolytic or photocatalytic water splitting is one of the interesting paths to contemplate both energy conversion as well as scalable storage. The former involves redox reaction of water to generate $H_2$. Hydrogen is known as an ideal green fuel for storage and supply due to its clean and high energy density. Therefore, the production of hydrogen fuel through water splitting using renewable energy sources to some extent can boost the effective utilization of renewable energy. Nevertheless, affordable hydrogen generation through energy intensive water splitting process can only be achieved with efficient, inexpensive and durable catalyst which can curtail energy barriers associated with electro- and photo-chemical processes. Although there are a number of noble metal-based precious catalysts are available in the market, a way forward in the development of affordable catalysts is the employment of metal chalcogenide based OER and HER catalysts for water splitting.

A number of metal chalcogenides have drawn considerable attention as catalysts for water splitting due to their affordability and better electrical conductivity relative to the metal oxides and noble metals. Accordingly, a number of strategies have emerged for enhancing the performance of metal chalcogenide catalysts for water splitting (both HER and OER). These strategies include anion/cation doping, phase tuning or engineering, heterostructures and hybrid materials, etc.

Atomic doping can alter the electronic structure, surface composition of the catalysts and adsorption energy of intermediates. These modifications optimize the catalytic activity through the optimization of free energy barrier and reaction mechanism. Adopting this approach,

$Co(Te0_{.33}Se_{0.67})_2$ has been demonstrated as OER catalyst with a low Tafel slop of 44 mV dec$^{-1}$, a overpotential of 272 mV at 10 mA cm$^{-2}$ and a durability of 50 h, while $Co(S_{0.72}Se_{0.28})_2$ owns better HER performance with a minimum slope of 80 mV dec$^{-1}$ and overpotential of 62 mV [14]. The outcomes can be attributed to structural defects driven active sites. Phase engineering has been implemented in $MoS_2$ where it has been found that 1T $MoS_2$ demonstrated better electrocatalytic performance due to higher electrical conductivity. The subsequent Cu@$MoS_2$ HER catalyst fabricated by doping Cu in 1T $MoS_2$ exhibited a low overpotential of 131 mV at the current density of 10 mAcm$^{-2}$, a Tafel slope of 51 mV/dec, and better stability [15]. Heterostructures enhance catalytic performance due to increased number and stability of active sites through synergistic effect of different components at the interface. Accordingly, nickel nitride/sulfide (NiNS) [16] has been employed as a HER and OER electrocatalyst for water splitting with the current densities of 48.3 and 12.4 mA cm$^{-2}$ at 1.8 V in seawater and neutral media. The $Ni_3N$ and Ni3S2 interface encourage both adsorption and dissociation of water. Similarly, $MoS_2$/SiCnw catalyst exhibited a low Tafel slope of 55 mV/dec [17]. Similarly, hybrid materials such as NiFe hydroxide/$Co_9S_8$/carbon cloth [18] and $Ni_3S_2$/$VS_4$ nanohorn on nickel foam (NS-horn/NF) [19] have been used an electrocatalyst with excellent performance. However, metal chalcogenides have to go a long way before they can be implemented as commercial catalyst for various reasons. The latter include development of metal chalcogenides as multi-functional catalysts, reconstruction problem of metal chalcogenides and underlying reaction mechanisms of electrocatalysis needs to be studied thoroughly to encounter bottlenecks. Furthermore, preparative methods for large scale synthesis of metal chalcogenides for industrial purpose needs to be developed.

## Thermoelectric Applications

Over the past decades, research on thermoelectric materials have attracted tremendously as the conversion of waste heat into electricity can be realized through simple device structure. The thermoelectric conversion efficiency can be estimated by the figure of merit ZT = $S^2\sigma T/\kappa$ (where S, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolutetemperature, and thermal conductivity, respectively). The performance of different thermoelectric materialscan be assessed by the thermal conductivity (κ) and power factor ($S^2\sigma$). At present, the need of the hour is to develop affordable, efficient and environmentally benign thermoelectric materials comprising of earth abundant elements. The performance

of these materials, further can be improved through tailored nanostructures [7]. One of the best fits to such type of materials are metal chalcogenide semiconductors owing to their high ZT values [20]. The latter may be attributed to low thermal conductivity of metal chalcogenides due to weaker covalent bonding and higher atomic weight compared to other materials [21]. Moreover, the electronic structuresand physiochemical of metal chalcogenides can be altered throughtheir size and shape engineering and chemical doping. A general strategy to improve ZT value of the materials is to reduce thermal conductivity and increase the electrical conductivity. A successful demonstration of this strategy can be seen 2D layered nanostructures where thermal conductivity is reduced due latticescattering of the phonons at the grain boundaries [22].

Accordingly, a number of strategies have been developed over the years. Among them, solution-based synthesis is the most viable method for material scalability and for tuning the kinetic and thermodynamic parameters for controlling the formation of targeted products under reasonably mild conditions. Solution based approach for metal chalcogenide-based materials include top-down liquid exfoliation method and bottom-up solvothermal, thermolysis or wet chemical methods. Top-down liquid exfoliationmethod is known for producing highly crystalline 2D transition metal dichalcogenide nanomaterials with good yields and in scalable amounts under mild conditions [23,24,25]. The former technique adopts shearing or ultrasonication of passivated layered materials to produce 2D nanosheets. For instance, $Bi_2Te_3$ and $Bi_2Se_3$ nanosheets were made by lithium intercalation and exfoliation of respective bulk materials [26]. Recently, S-doped SnSe nanosheets were produced by hydrothermal lithium intercalation and subsequent exfoliation from bulk ingots [27]. S-doping effectively reduced thermal conductivity via enhanced phonon scattering resulted from atomic disorders and nanosized boundaries. Thermal conductivity further lessened in porous $SnSe_{1-x}S_x$ nanosheets which had been attributed to the nanoscale porous boundaries. These nanosheets exhibited a ZT value of 0.12 at 310 K. Turner et. al. isolated $Bi_2Te_3$nanosheets of thickness 15 ± 8 nm via ionic liquid exfoliation of nanoplatelets [28]. For promising large-scale exfoliations, electrochemical exfoliation can be adopted. For example, electrochemistry has been employed for the exfoliation of layered $Bi_2Te_3$[29]. In addition to exfoliation method, nanostructured metal chalcogenides such as $Bi_2Te_3$ [30], $Cu_2Se$ [31], and SnSe [22] were synthesized via solvothermal method. $Cu_2Se$ pellets exhibited ZT of 1.82 at 850 K owing to an ultralow thermal conductivity as a consequence of strong phonon scattering at grain boundaries [31]. Further, rare-earth
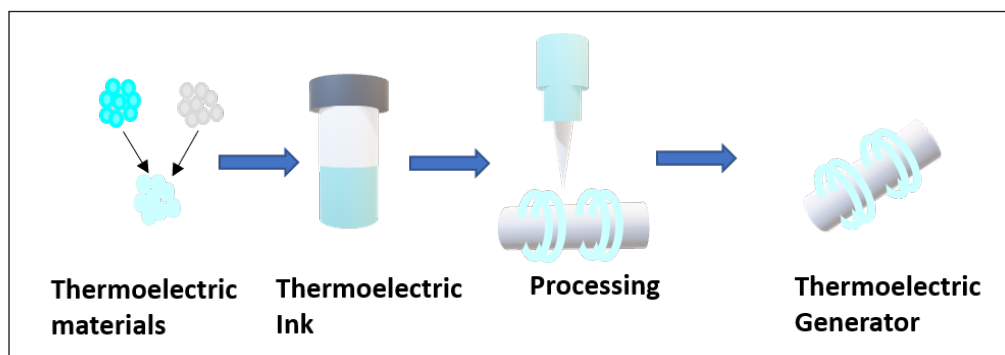
*Figure 1 Schematic diagram forthermoelectric generator (TEG) fabrication by ink-based process.*

doped $Bi_2Te_3$nanopowders showcased a ZT value up to 1.29 at 373 K [30]. Other than solvothermal method, co-precipitation synthesized of $Cu_2Se$ nanoparticles showed an excellent ZT value of 1.35 at 850 K [32].

In addition to the above methods, template-assisted, chemical reduction–precipitation and electrodeposition methods have also been employed for the synthesis of metal chalcogenides such as $Bi_2Te_3$, $Cu_2Se$, SnSe and $Bi_2Se_3$ nanostructures. Moreover, ink-based processing methods (Figure 1) have also been developed for cheaper and large-scale thermoelectric device fabrication.

The thermoelectric properties of metal chalcogenide nanostructures prepared by different strategies are documented in various reviews [7,33].

## Energy Storage Applications

Demand and development of sustainable energy systems requires efficient energy storage systems such as lithium-ion batteries (LIBs), sodium-ion batteries (SIBs) and supercapacitors (SCs), etc. Metal chalcogenide-based materials are one of the best electrode materials which have been widely used for the latter applications due to high reversible capacity, a substantial number of electroactive sites, cyclability and durability. Improving the performance of these devices in terms of energy density, rate capability, cycling and safety is critical to extend and expand their practical applications. Therefore, lot of efforts have been focused in this direction.

## Rechargeable Alkali metal-ion Batteries

Among the various energy storage devices, rechargeable lithium-ion batteries (LIBs) (Figure 2) are widely deployed as portable electronic storage devices and have been extensively studied due to their high energy density, durability, wide operation temperature ranges and memory effect free characteristics. While sodium-ion batteries (SIBs) have drawn extensive attention as potential candidate for grid energy storage owing to abundant nature of sodium and an alternative to LIBs. The extension of their practical applications and large-scale deployment critically dependent ontheir performance with consistent safety. Therefore, development of affordable electrode materials for high-capacity, fast charging, and durable batteries is inevitable. Accordingly, metal chalcogenide-based electrode materials have been developed. The former possesses higher theoretical specific capacities for LIBs/SIBs relative to other traditional intercalation electrode materials [34].

For example, $FeS_2$ displayed a theoretical specific capacity of 894 mAhg$^{-1}$ as LIB cathode, which is much higher than that of $LiMO_2$ intercalation cathodes (M = Mn, Ni or Co) [35]. Additionally, faster charge transfer kinetics in metal chalcogenides makes them more electrochemically reversible relative to metal oxides. Nevertheless, intricacies such as shuttle effect of lithium/sodium polysulfides, volume expansion of electrode materials due to alloying/dealloying processes and other unproductive electrocatalytic properties pertaining to metal chalcogenide applications as battery electrodes remain.

LIBs are engrossed on transition metal sulfides like cobalt-, iron- and nickel-sulfides. Whereas the storage of Na-ions in metal sulfides rest on the type of constituent transition metal elements in these metal sulfides. The performance of these batteries further enhanced in several ways which include nanostructurization of electrodes, increasing the conductivity and buffering the volume expansion through carbonaceous material coatings or composites of metalchalcogenides, etc. Further, the migration rate of alkali ions can be improved in layered like structures. Recently, it has been verifiedthat doping with cations or heteroatoms can advance the lithium storage kinetics of metal chalcogenide electrodes. The defects and local charge polarization resulted as a consequence of doping are important in improving charge and electron transport [36]. For example, N-doped carbon materials enhance electrode cycle performance through chemisorption for poly-sulfides while S-doping increase conductivity due to stronger electron donor ability of S [37]. Besides doping, employment of carbon composites as electrodes boosts LIB performance owing to their excellent electronic conductivity, large surface area and buffer for

volume expansion problems. For instance, g-$C_3N_4$@$WS_2$ composite, delivers a high discharge capacity of 1136.1 mAh/g at 0.1 C and exceptional cycling stability of 433.8 mAh/g after 1000 cycles [38]. Moreover, hierarchical porous structuresboost Li$^+$ transport properties causingan increased rate capacity [38,39]. Recently, MOF derived chalcogenides showcase excellent rate capacity due to their inherent porous structure.

SIBs have emerged as potential energy storage substitute due to their high theoretical specific energy density (760 Wh/kg), cost-effectiveness, excellent cycle stability and low redox potential [37,40,41]. Yet their development is hampered due to problems like high atomic weight of Na resulting in relatively lower mobility with respect to Li and safety issues pertaining to low standard electrochemical potential. Additionally, dendrite structure formation to accommodate large volume change, high reactivity driven electrolyte degradation and mechanical stress as a consequence of larger Na$^+$ radius severely affect the performance of SIBs. Therefore, metal chalcogenides have been employed as SIB electrode material due to their exceptional theoretical capacity, thermodynamic stability and redox reversibility. Tailor made nanostructures including hollow structures, doping and composites further enhance the efficacy of SIBs. To counter various SIB issues, hydrothermally prepared bimetallic $Fe_7Ni_3S_{11}$ nanoparticles confined with nitrogen-doped carbon employed as SIB electrode exhibited a reversible specific capacity of 567 mAh/g at 0.2 A/g. Also, a heterojunction bimetallic sulfide nanosheet $SnS_2$/$FeS_2$/rGO fabricated SIB electrode exhibited a capacity of 768.3 mAh/g at 0.1 A/g and 541.2 mAh/gat 1 A/g [42]. Furthermore, $NiSe_2$@ Boron carbonitride nanotubes composite [43] made anode exhibited exceptional reversible storage capacity of 787

mAhg$^{-1}$ at a current density of 100 mAg$^{-1}$ and enhanced cycle stability of 382.4 mAh g$^{-1}$ at 2 Ag$^{-1}$ after 2000 cycles.

In addition to LIBs and SIBs, metal-sulfur and metal-air batteries have also garnered significant attention due to their enormous potential in electrochemical storage systems. However, metal-sulfur batteries suffer from polysulfide shuttling effect. To counter this problem, transition metal dichalcogenide based materials such as $MoS_2$ nanoflakes and $MoS_{2-x}$/rGO composites were employed as a catalyst to convert polysulfides into a sulfur cathode [44]

## Supercapacitors

Among the different energy storage systems, supercapacitors (SCs) have been in focus owing to their excellent fast charging-discharging, high power density, cycling characteristics and environmental safety. However, practical engineering applications of super capacitor is restricted by limited energy density as a consequence of charge accumulation on the electrode surface. Therefore, a number of studies have been dedicated towards achieving high energydensity yetupholding its power density and cycle durability. Of these, progress of effective electrode materials evades these problems. Metal chalcogenides have been established as promising candidates for storage devices due to outstanding reversible redox mechanisms and higher charge/energy density relative to other commercialized electrode materials.

Especially, employment of transition metal chalcogenides (TMCs) such as ME or $ME_2$ (M = Ni, Co, Mn, Cu, Zn, Mo or W, E = S, Se or Te) as super capacitor electrodes unveiled promising performance with respect to stability and energy density by virtue of the copious redox-active sites, variable oxidation states, decreased bandgap, and substantial electrical conductivity [45]. Additionally, faster ion transport kinetics enhances the electrochemical properties.

Chalcogenides function on two storage mechanisms viz. a pseudocapacitive (fast reversible redox mechanism) or hybrid (combination of charge accumulation and fast reversible redox mechanism). Accordingly, capacitors have been categorized as pseudocapacitors and hybrid capacitors. Pseudocapacitors are promising energy storage system candidates due to their greater specific capacitances. Amid all nanostructured electrodes, transition metal chalcogenide-based materials have been recognized as futuristic electrode materials for the former devices, owing to their ample electroactive sites and better electrical conductivity. To counter limitations posed by rechargeable batteries and traditional SCs transition,
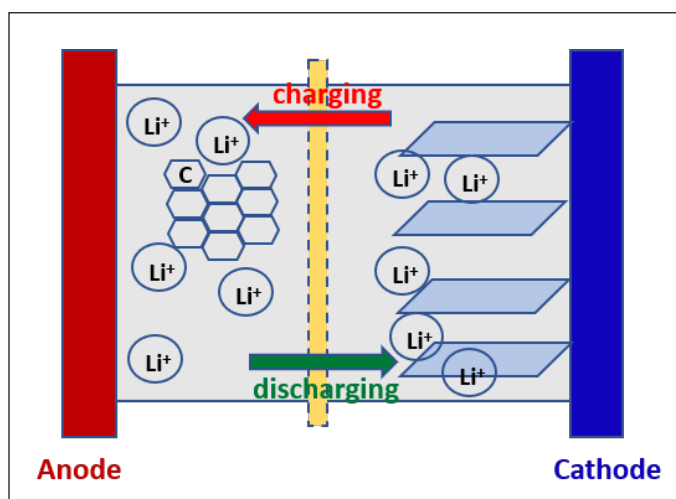


*Figure 2 Schematic diagram of LIB structure and working mechanism.*

transition metal hybrid capacitors have been developed as a part of highly efficient energy storage devices by virtue of their outstanding electrical conductivity and electrochemical activity. Particularly, cobalt and nickel-based transition metal chalcogenides have been employed as quality electrode materials in hybrid capacitors. For example, NiS@Ni delivered an exceptional specific capacitance of 1109 C/g at a 2 A/g, as a potential hybrid-capacitor positive electrode [46]. Similarly, $Ni_xCo_{1-x}Se_2$ nanotubes [47] exhibited a high specific capacitance (1157 F/g at 1 A/g) due to synergistic effect of Ni and Co ions.

Despite of excellent electrochemical activity of various chalcogenides, short falls such as low conductivity, a low surface area and poor cyclability hampers their progress. A number of methods have been employed to create nanostructures of high surface. Similarly, ternary metal chalcogenide hybrid supercapacitors (MX; M = Zn–Co–Ni; X = S, Se, Te) were made [48]. Besides, shape engineered materials and nanocomposites employing different synthesis protocols have also been investigated to modify specific capacitance. For instance, lower electronic conductivity of $MoS_2$ has been countered by this strategy [49]. $WS_2$/-$NiMoO_4$ composite electrodes [50] showcased better performance due to better pore size, electrical conductivity and stability. Furthermore, transition metal sulphides with weaker M-S bond have been in focus owing to their high capacitance prediction. All the above studies clearly underpin the importance of synthesis methodologies and materials to improve the performance of supercapacitors.

In addition to aforementioned devices, technological advances gave impetus to flexible supercapacitors. For the latter applications high power density, long cycling stability, and excellent mechanical integrity are inevitable. Moreover, the electrolyte, separator and electrodes must withstand high mechanical stress. For example, an electrode fabricated by copper sulphide/zinc sulphide/porous carbon composite [51], delivered an extraordinary electrochemical performance as a flexible SC.

## Conclusion and Future Prospects

Applicability of metal chalcogenides has witnessed significant boost recently due to their fascinating intrinsic properties coupled with tailor made properties. However, the future prospects for metal chalcogenides rely on the development of synthetic protocols for phase pure materials in bulk quantities with better reproducibility and yield. The rationale behind this is that the applications are dependent on material properties which in turn rely on size, shape, phase and composition, etc. Therefore,

synthetic strategies for custom-made materials in scalable quantities are need of the hour.

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**Dr. G. Kedarnath,** *Scientific Officer (G), joined BARC in the year 2000 after graduating from BARC training school. He has been working on designing and development of single source molecular precursors for metal chalcogenide nanomaterials and thin films. He was awarded Ph. D. (Chemistry) in 2010 by University of Mumbai. He pursued his post-doctoral research at Virginia Commonwealth University, Richmond, USA. He has published more than 50 papers in peer-reviewed journals. He is also a reviewer of ACS, RSC and Elsevier publishers. He is a recognized Ph. D. (Chemistry) guide of HBNI and is a recipient of Scientific and Technical Excellence Award of DAE in 2013.*

# A mini review on metal chalcogenides as anode material for Li ion battery

**Dipa Dutta Pathak, Kruti K. Halankar and B. P. Mandal***
*Chemistry Division, Bhabha Atomic Research Center, Mumbai, India*
*Homi Bhabha National Institute, Anushaktinagar, Mumbai, India*
*Email: bpmandal@barc.gov.in*

## Abstract

Metal chalcogenides have emerged as potential candidate for anode material for lithium ion battery with higher energy and power density. The chemistry of metal chalcogenides is very rich due to unique crystal structure. In the present article, the lithium storage capabilities of different chalcogenides have been summarized.

## Introduction

Lithium ion batteries are the suitable choice to combat problem arises due to environment pollution and to meet futuristic energy demand for electric vehicle. In order to develop efficient batteries, the energy density, power density cycle-ability etc. of the individual electrodes of batteries should be high. Presently, graphite is used as anode material in commercial lithium ion batteries, however, due to its lower capacity (372 mAh/g) and slow charge discharge rate, it needs to be replaced with anode material with high energy and power density. Chalcogenide based anode materials are excellent options for futuristic batteries. The capacity of metal chalcogenides is found to be much higher than graphite. A huge volume of research can be found in literature on metal chalcogenides. [1-5] Transition metal chalcogenides crystallizes in different structure depending upon metal and chalcogen ratio. The electrochemical performance also varies accordingly. Mostly, the chalcogenides are nonconducting, therefore, it is important to add conducting agents like, CNT or conducting carbon or graphene to improve the overall conductivity of the composite. The additive gives extra cushion to take care the strain arises due to volume variation and required electronic conductivity. Different routes have been adopted in recent past to synthesis these metal chalcogenides like sol-gel, hydrothermal, solvothermal etc. Interestingly, synthesis form single source precursor results chalcogenides with different metal to chalcogen ratio by changing the coordination capability of the solvent. In this mini review the electrochemical performance of different metal chalcogenides has been summarized.

## Metal sulfides

Metal sulfides are widely reported in literature as anode material for lithium ion battery compared to other chalcogenides due to relatively easier synthesis process, lower cost and lower mass than other chalcogenides. Also,

the metal sulfides bonds are relatively weaker compared to metal oxygen so it is better to use them as reversible anode material. Different metal sulfides and selenide have been discussed in next sections.

## Nickel sulfide

Several kinds of nickel sulfides depending upon Ni: S ratio have been reported as anode material for lithium ion battery. Mostly conductive carbonaceous matrix is used to cover the particle to reduce the strain caused due to volume variation during lithiation and delithiation. Among them $Ni_3S_2$ has been prepared in presence of porous graphene oxide by Zhang et al. [6]. This material shows around 830 mAh/g capacity at 100 mA/g current density. The authors have observed in $Ni_3S_2$/GO composite $Ni_3S_2$ particles get anchored on GO sheets. The GO sheets offer required electronic conductivity during cycling. The material exhibits 1150 mAh/g capacity cycled after 500 loops at 1 A/g current density.

Among other nickel sulfides, $NiS_2$ has been prepared from decomposition of Ni based MOF in presence of sulfur. The resultant hollow $NiS_2$ shows higher capacity as well as higher rate capability than agglomerated analogue. The hollow $NiS_2$ exhibits around 600 mAh/g capacity at 1 A/g current density after 600 cycles. On the other hand, the agglomerated one demonstrates 100 mAh/g after 400 cycles. Therefore, it can be summarized that in case of this type of materials, presence of carbonaceous material is very crucial. [7]

Cyclic voltammetry (CV) is well known method by which lithiation/delithiation mechanism can be understood. CV on $NiS_2$ demonstrates that initially lithiation takes place at 1.67 V and form $Li_xNiS_2$ which on further lithiation results decomposition of $Li_xNiS_2$ into $Li_2S$ and Ni at 1.25 V. On charging the nickel nanoparticles get lithitated at 2 V and 2.28 V via formation of $Li_xNiS_2$ complex. The hump shown in first discharge at 0.74 V

arises due to SEI (solid electrolyte interface) layer formation because the peak can not be observed in second cycle onward. The formation of SEI layer on anode material is very important because it protect the material for further degradation. All the peaks, except the SEI peak, in cathodic as well as in anodic cycles could be observed in second cycle onward.

## Cobalt sulfide

Coblat sulfides also exists in different forms like $CoS_2$, $Co_2S_3$, CoS, $Co_9S_8$ etc depending upon different synthesis conditions, these materials can be synthesized. These cobalt chalcogenides have been used as anode materials for lithium ion battery. Cobalt sulfide in presence of reduced graphene oxide exhibits excellent electrochemical performance. $Co_{1-x}S$/rGO composite shows around 700 mAh/g capacity at 2.5 A/g current density. Lithium diffusion coefficient has been calculated in the sample and it is found to be around $10^{-12}$ cm$^2$/s. [8] Instead of graphene, carbon has also been used as additive for $Co_9S_8$ coverage. After dispersion of $Co_9S_8$ on carbon, the overall conductivity increases [9]. Reversible capacity of $Co_9S_8$@ carbon is found to be around 595mAh/g after 160 cycles at 0.2 A/g current density. The material regains its initial electrochemical performance after cycling at higher current density.

## Copper sulfides

Copper sulfide are also excellent anode material for lithium ion battery. $Cu_xS$ exists in a number of different crystallographic phases depending upon Cu: S ratio in the structure. They differ in the location of Cu and S which changes as a function of copper and sulfur ratio. Among all the phases of CuxS, digenite ($Cu_{1.8}S$), one of the copper-rich sulfides, is considered as a favourable candidate for battery electrode materials due to (i) the stable crystallographic form which is desirable for active materials for LIBs, (ii) the sole presence of the covalent Cu–S linkage and the absence of a direct S–S bond, and (iii) its narrow band gap (1.2 eV) which leads to better electronic conductivity. [10] The materials in nanoform provides better results than the materials at bulk form. Also, conductive additive like carbon or rGO provides support to CuS to perform better. $Cu_{1.8}S$ delivers 462 mAh/g capacity and retains capacity 240 mAh/g even after 300 cycles at 0.1 A/g. Capacity were measured at different current density and it was found initial capacity could not be retained after passing through high current. [11]

## Tin Sulfide

Another important material as anode for lithium ion battery application. The SnS synthesized by precursor method initially shows capacity as high as 800 mAh/g



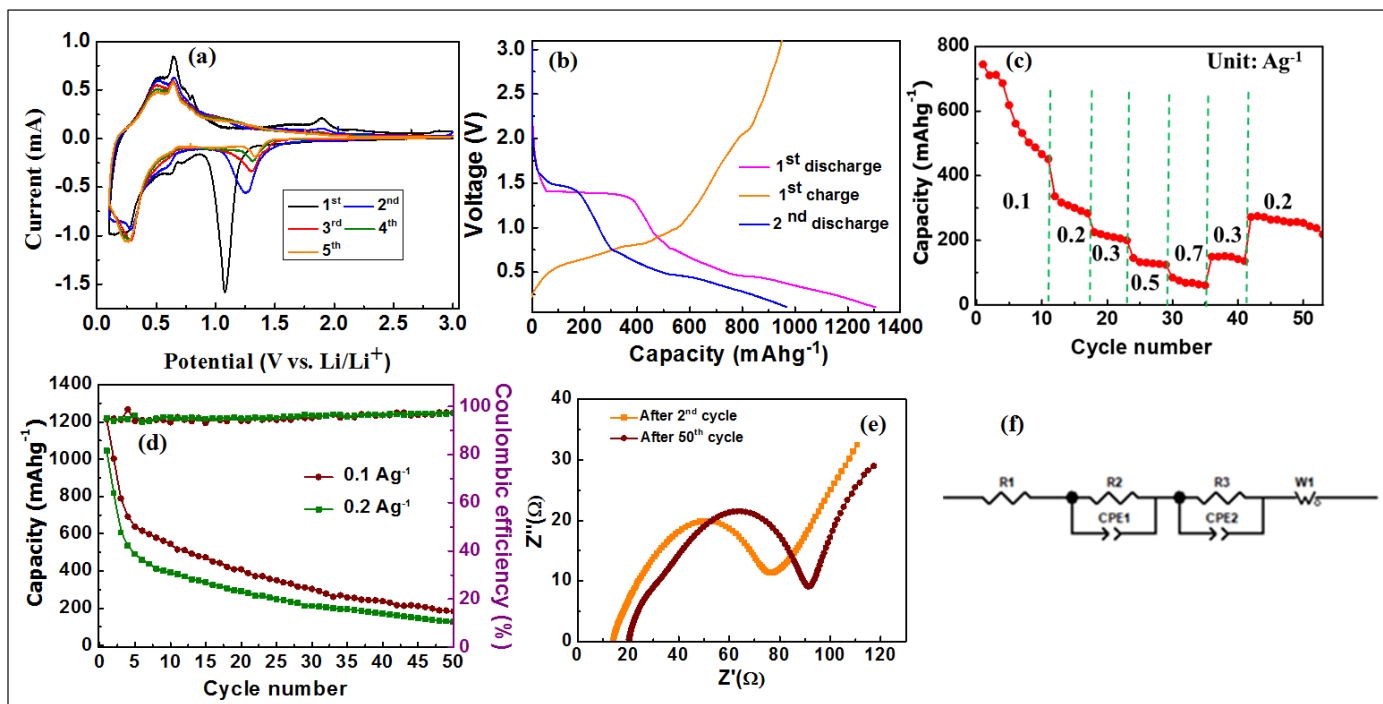**Figure 1:** *(a) Cyclic voltammetry curves of the SnS anode at the scan rate of 0.1 mVs$^{-1}$(b) charge discharge charging–discharging voltage profile at 50 mAg$^{-1}$ current density (c) Rate performance of the electrode at increasing current density from 0.1 Ag$^{-1}$ to 0.7 Ag$^{-1}$ (d) Long term cycling performance of SnS (e) Nyquist plots of SnS after 2nd and 50th cycle (f) model used to fit the Nyquist plots. [12]*

at 0.1A/g current density which decreases slowly and shows around 200 mAh/g after 50 cycles. The impedance measurements have been done on the samples after running 2nd cycle and 50th cycle. The Nyquistic plots have been fitted with the circuit given in Figure 1. [12]

Electrolyte resistance increases with cycling due to decomposition of electrode material. Increase in resistance causes deterioration of electrochemical performance.

## Iron sulfide

Theoretical capacity of iron sulfide is 609mAh/g. Reversible capacity of iron sulfide is 780 mAh/g can be obtained at 0.5 A/g current density. The improved performance is due to addition of carbon nanosheets which increases the point to point contact between electrolyte and electrode material. Moreover, the dissolution of polysuflides decreases in carbon wrapped sample. [13] Tour et al. addressed the stability issue in FeS-graphene composite and found that the dissolution of polysulfide diminiseh in the composite form and the reversible capacity is found to be 530 mAh/g after 100 cycles at 0.4 A/g current density. [14]

## Molybdenum sulfides

Among chalcogenides, probably $MoS_2$ and $WS_2$ has been investigated intensively. Bare $MoS_2$ can not be cycled for long run as anode material. However, Halankar et al reported that its performance can be increased just by adding 8% carbon with it [Figure 2]. Using EXAFS and XANES, they have detected the formation of $Li_xMoS_2$ complex as an intermediate during lithiation. Upon further lithiation $Li_2S$ and Mo nanoparticle forms over $Li_2S$ which increases the conductivity also. [15]

## Metal Selenides

Metal selenides are also studied with great intense though energy density and power density are found to be lower in comparison with metal sulfides due to higher atomic weight of selenium than sulfur. Among metal selenides, Indium selenides, tin selenides etc. have been used in recent past anode material for lithium ion battery.

## Indium selenides

Karmakar et al. reported synthesis of cubic InSe and hexagonal $In_2Se_3$ through proper choice of coordinating solvents from a structurally characterized air and moisture stable single source molecular precursor: *tris*(4,6-dimethyl-2-pyrimidylselenolato)indium(III). [16] The electrochemical performance of $In_2Se_3$ is found to be better than cubic InSe. $In_2Se_3$ exhibits around 200 mAh/g capacity at 1 A/g current density with coulombic efficiency. However, the performance of InSe degrades very fast at higher current density. The lithiation and delithiation mechanism of two selenides are found to be slightly different.

## Tin Selenides

Tin selenide is an excellent choice as anode material for lithium ion battery. The Coulombic efficiency decreases with cycling because of degradation of SnSe upon cycling. [17] The first cycle charge discharge capacity was found to be 1134 and 809 mAhg-1 at 50 and 100 mAg-1 respectively. After 70 cycles, the cell could retain its capacity at 400 mAh/g at 50 mA/g current density. The cell fabricated with SnSe as anode material were tested at different current density raning from 50 mA/g to 400 mA/g current density. The capacity decays at higher current and could revive partially when subjected at lower current density.
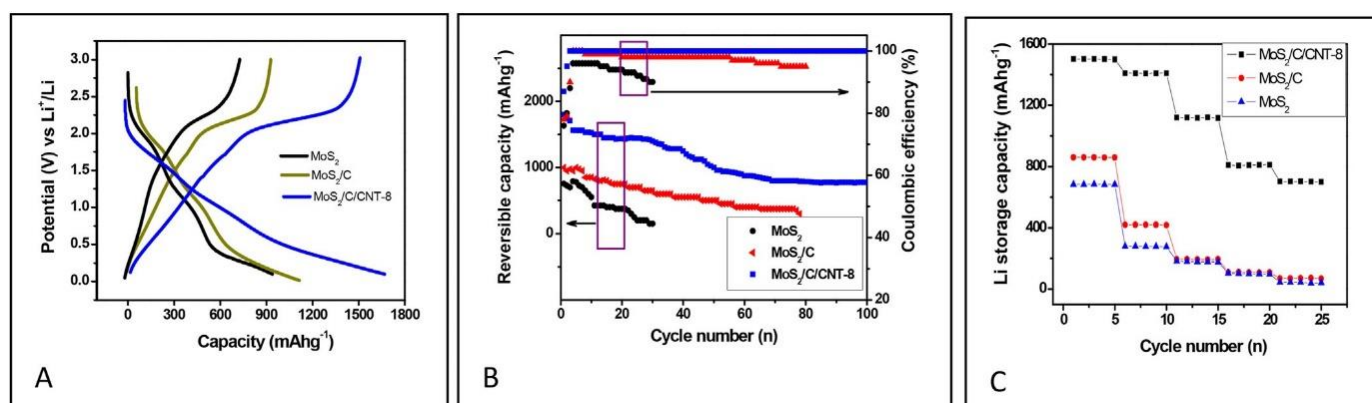


**Figure 2.** *(A) First cycle galvanostatic discharge/charge curves obtained with pristine $MoS_2$, $MoS_2/C$ and $MoS_2/C/CNT-8$ when cycled against Li at current density of 100 mA/g. (B)Cyclic stabilities of the pristine $MoS_2$, $MoS_2/C$ and $MoS_2/C/CNT-8$ electrodes, as recorded at a current density of 100 mA/g. (C) Electrochemical performance of $MoS_2$-based electrodes upon galvanostatic cycling at different current densities. [15]*
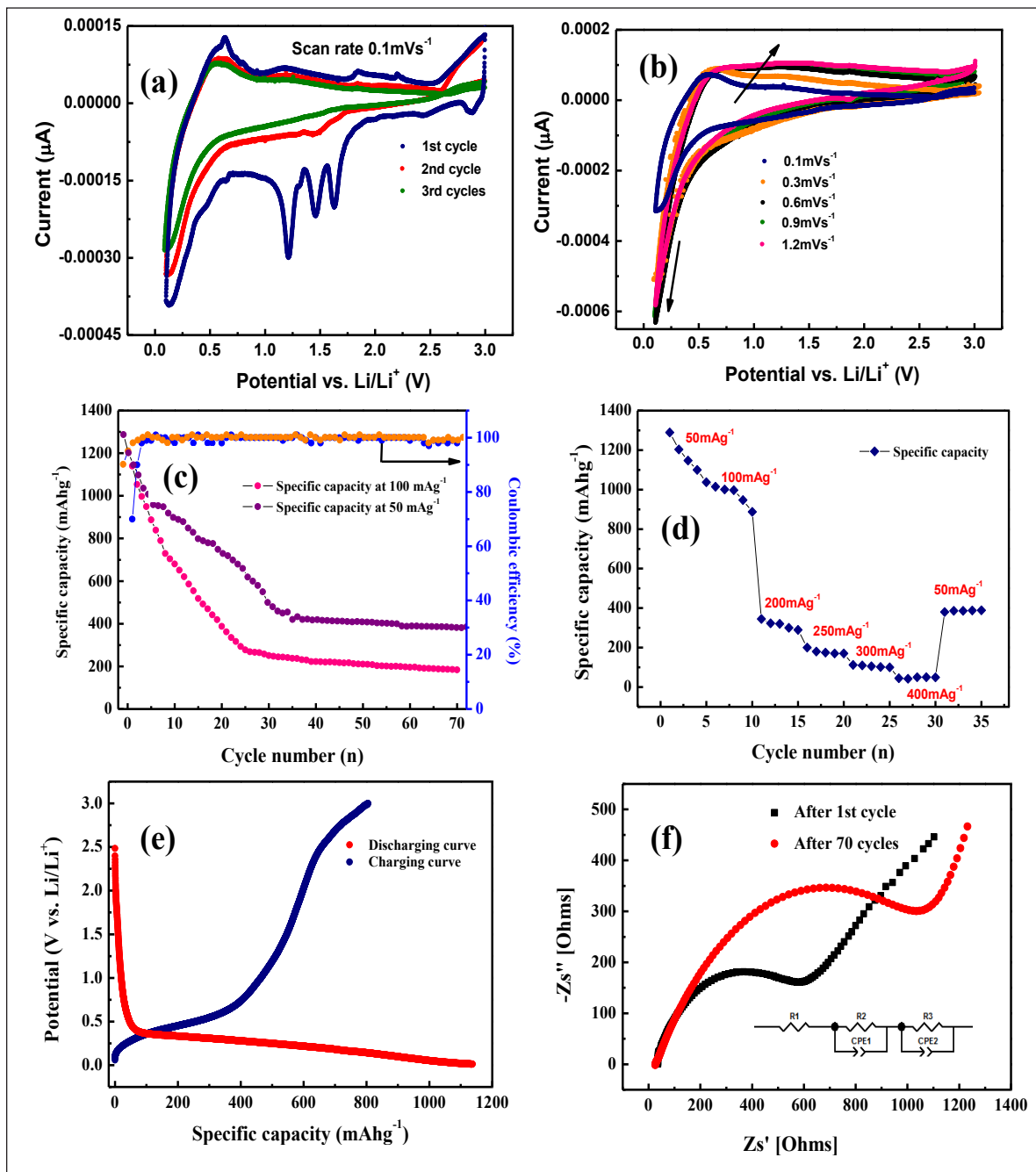
*Figure 2: (a) Cyclic voltammogram of SnSe (obtained from pyrolysis) between 0.1 to 3.0 V at 0.1 mV/s, (b) different scan rate cyclic voltammograms, (c) cycling and coulombic efficiencies of electrodes at 50 and 100 mA/g current density, (d) specific capacity at different current densities, (e) first charge discharge profile between voltage ranging from 0.01 to 3.0 V at 100 mA/g, (f) Nyquist plots of SnSe after the 1st and 70th cycle with the model used to fit the plots [17]*

The lithiation mechanism could be studied using cyclic voltammetry. The cathodic peaks at ~1.63, 1.46, 1.2 V have been assigned to formation of $Li_xSnSe$ and then decomposition to $Li_2Se$ and Sn. and anodic peaks appear at ~0.63, 1.16, 1.84, 2.19 V. The first three reduction peaks observed in first cycle correspond to lithiation of SnSe ($Li_xSnSe$) and decomposition of $Li_xSnSe$ to $Li_2Se$ and Sn

($SnSe + Li = Li_xSnSe = Li_2Se + Sn$). The reduction peak at ~0.6 V is ascribed to the formation of solid electrolyte interface (SEI) layer. there is signature of alloying of Li and Sn in next step. In the anodic scan the peak at 0.6 V is attributed to the dealloying of $Li_xSn$ to Li and Sn. The other two peaks at 1.16 and 1.84 V corresponds to the reaction of $Li_2Se$ and Sn which forms SnSe ($Li_2Se + Sn = $

SnSe + Li). In the next cycles, cathodic peak appear at 1.86 V and anodic peaks appear at ~1.2, 1.85 V. The cathodic peak (1.86 V) corresponds to the lithiation of SnSe and formation of $Li_2Se$ and Sn. In the next anodic sweep, the peaks at 1.2 and 1.85 V correspond to delithiaiton of $Li_2Se$ and formation of SnSe and Li. There is a slight shift in the peak position with increase in the number of cycles that was observed from the CV.

## Metal tellurides

Metal tellurides are scarcely reported in literature because of low availability of tellurium and difficulty in synthesize. However, recently, it has been reported that some metal tellurides are excellent anode material. Among the chalcogenides, band gap decreases with increase in atomic weight of the chalcogen. Therefore, tellurides are inherently found to be better electronic conductor which is one of the pre-requisites for a material to be regarded as anode for lithium ion battery. Mostly, physical mixture followed by heating in vacuum or inert atmosphere is done to synthesize the tellurides. However, synthesis by single source precursor route is one of the advantageous one as many polymorphs can be obtained by this route. In this case also the lithiation takes place by conversion and alloying mechanism. [18, 19]

## Conclusions and outlook

Metal chalcogenides are an excellent class of material to be used as anode material for lithium ion battery. However, these materials need some additives to further increase the conductivity and take care the volume variation. Lithiation and delithiation mechanism is mostly conversion as well as alloying type. The capacity of these materials could be improved by nanostructuring the bulk counterpart. Further, some chalcogenides can be prepared by 2D form also and it is expected that in 2D open form the energy density will be far better. Further fundamental research is required to achieve maximum efficiency in energy storage.

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| | *After completing her M.Sc. in Physics from Banaras Hindu University, Dr Dipa Dutta Pathak received her Ph.D in Materials Science from Indian Institute of Technology Bombay in 2017. She has been awarded the "Excellence in Thesis Work" from IIT Bombay for outstanding research contribution. As part of her post-doctoral research she worked on development of cathode material for L-S batteries, as SERB-NPDF till 2019. She is currently working as a DST INSPIRE faculty at Bhabha Atomic Research Centre. Her research interests include design and fabrication of electrode materials of Li-ion and Li-S batteries. Her research findings have been published in reputed peer-reviewed international journals and well-received.* |
| | *After completing MSc from Mumbai University, Kruti K. Halankar joined BARC for PhD. She completed her PhD from BARC on electrode materials for Li-ion battery. She has owned several awards like ACS Best presenter Award. Presently she is working as Post doc fellow in University of Cologne, Germany* |
| | **Dr. B. P. Mandal** *completed MSc from University of Burdwan, West Bengal in 2003. He was awarded the PhD degree in Chemistry in 2009 by Mumbai University. He did his postdoctoral research in development of new electrodes for Li ion battery at Wayne State University, USA. He was awarded DAE-Young Scientist award in 2012. He has been awarded membership of National Academy of Science, India and also he has received DAE-SSPS Young Achiever Award in 2017. Presently he is involved in development of battery materials. He has transferred the technology for synthesis of electrode materials for lithium ion battery to different Indian companies for commercialization. Dr. Mandal has been awarded with SMC Bronze medal in 2022. Dr Mandal has authored more than 90 scientific papers in the journals of international repute.* |

# DFT exploration of metal oxide and chalcogenides for Rechargeable Ion Batteries

**Sandeep Nigam\*, Adish Tyagi, B. P. Mandal, C. Majumder**
*Chemistry Division, Bhabha Atomic Research Centre, Mumbai*

## Abstract

Rechargeable Ion Batteries are key for electric vehicles market. Currently, electric vehicle (EV) batteries companies are looking for high energy density rechargeable-battery and making them easier and faster to charge and long-lasting. In this context, researchers are exploring various approaches to improve the energy density and recyclability of rechargeable ion batteries and special focus has been on phosphate and chalcogenides-based electrode material. Present article summaries our effort to investigate phosphate ($LiFePO_4$) and Chalcogenide ($Cu_{1.8}S$) electrode materials aiming towards improved electrochemical performance. The article discusses structure, electronic properties of hosts and characteristics of ion movement channel.

Low-cost batteries with high energy density and recyclability are utmost requirement of electric vehicles and towards the growth of renewable energy technologies. Deeper understanding of behaviour of electrode/electrolyte material under complex electrochemical environment is crucial for the development of next-generation rechargeable ion batteries. In this context, theoretical methods can not only provide the deeper understanding for rationalization of experimental observation, but it can guide the future experiment by its prediction. In the present work, we have investigated the two recognized electrode materials, phosphate ($LiFePO_4$) and Chalcogenide ($Cu_{1.8}S$) using DFT tools. In the subsequent section, we will present these studies. The inferior lithium-ion transmission capability and poor electronic conductivity of $LiFePO_4$ impede its commercial implication. With an aim to optimize the electrochemical behavior of $LiFePO_4$ by co-doping approach, theoretical work has been initiated on orthorhombic $LiFePO_4$.[1] calculations shown are performed within the Generalized Gradient Approximation GGA-PBE with the projector-augmented wave (PAW) method as implemented in the VASP. An energy cut-off of 400 eV and 3 x 3 x3 k-point mesh were found to be enough to converge the total ground state energy within 1 meV. Orthorhombic unit cell structure with space group $P_{nma}$ (No. 62) containing 28 atoms were used as initial structure for the calculations. The lattice parameters of the relaxed bulk $LiFePO_4$ structure are a=10.805 Å, b=5.741 Å, c=4.780 Å. Optimized structure was found to have $4m_B$ magnetic moment per formula unit cell. Non-magnetic structure ($0m_B$ magnetic moment per formula unit cell) is 0.82 eV higher in energy. The calculated band gap of was estimated to be ~2.8 eV, which

is smaller than the experimental value of 3.9 eV. Inclusion of U parameter (GGA+U) method resulted in bandgap value as 3.8 eV which is very close to the experimental value of 3.9 eV. The lattice parameter calculated at GGA+U levels are also reproducing the experimental values within the acceptable limit. The state near the fermi level has major contributions from Fe and O atoms. With an aim to optimize the electrochemical behaviour of $LiFePO_4$ by co-doping approach, $Y^{3+}$ and $Bi^{3+}$ ion was doped in orthorhombic $LiFePO_4$. Inclusion of co-dopant in $LiFePO_4$ results in increase of lattice parameter and hence the unit cell volume. Results indicate that doping of $Bi^{3+}$ in $LiFePO_4$ results in 4.4%, 5.3% and 0.3% increase in lattice parameter along *a*, *b* and *c* directions respectively. Bi doping cause modification in the local geometrical environment around vicinal $Li^+$ ion. The variation of dopant concertation from 3% to 6% shows increase in the lattice volume, for both $Y^{3+}$ and $Bi^{3+}$ doping with highest enhancement along *b-axis* of crystal along [010] direction. The extent of increase is more for $Bi^{3+}$ doping in contrast to $Y^{3+}$. Molecular dynamics simulation of $LiFePO_4$ at 300K shows that shared $LiO_6$ octahedron parallel to [010] direction got significantly distorted during the diffusion process. It is found that thermal energy induced distortion of $LiO_6$ octahedron, leads to movement of Li ions along [010] direction via a zig-zag path. Inclusion of dopant ion in the $LiFePO_4$ facilitates the distortion of $LiO_6$ octahedron due to increase in channel size along [010] direction.[2]

Recently Copper sulfides have been explored rigorously by researchers as alternative electrode materials for rechargeable batteries. It was found that cell based on $Cu_{1.8}S$ nanostructures have a high initial capacity

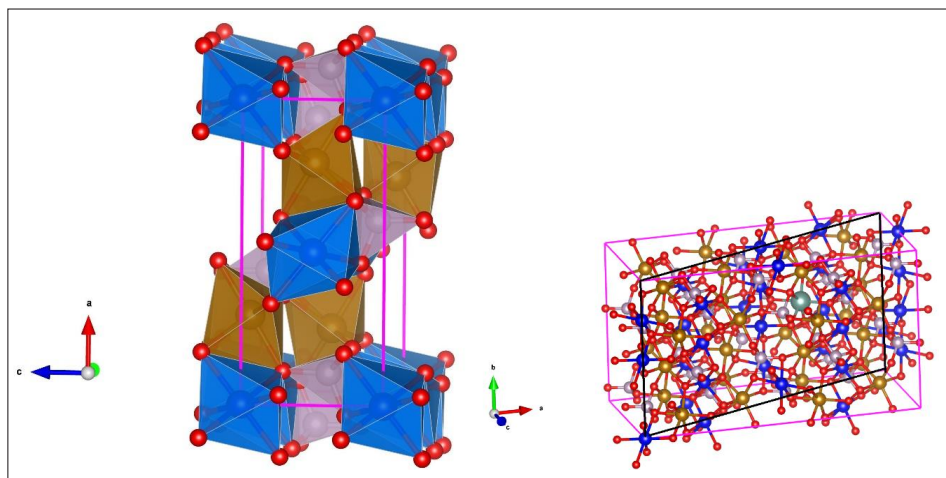**Figure 1**: *Polyhedra of LiFePO$_4$ and 010 plane in the structure.*
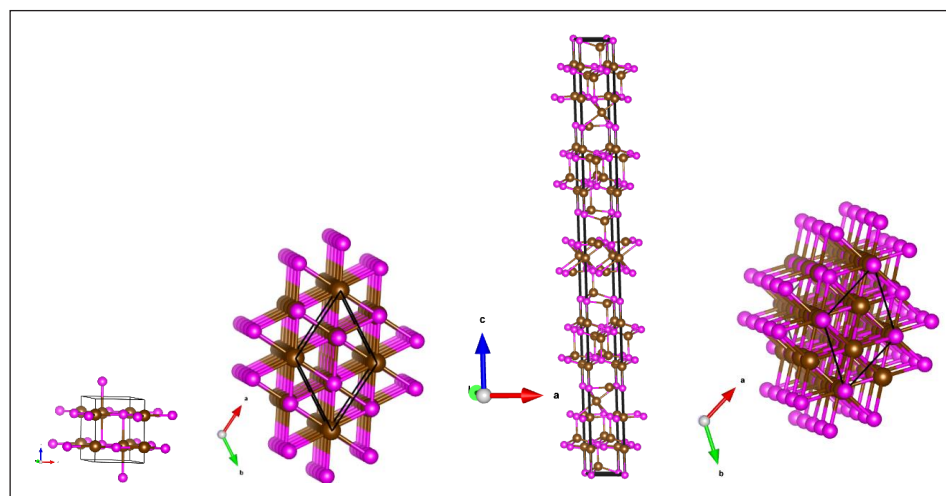


**Figure 2.** *Unit cell of hexagonal Cu$_2$S and rhombohedral Cu$_{1.8}$S*
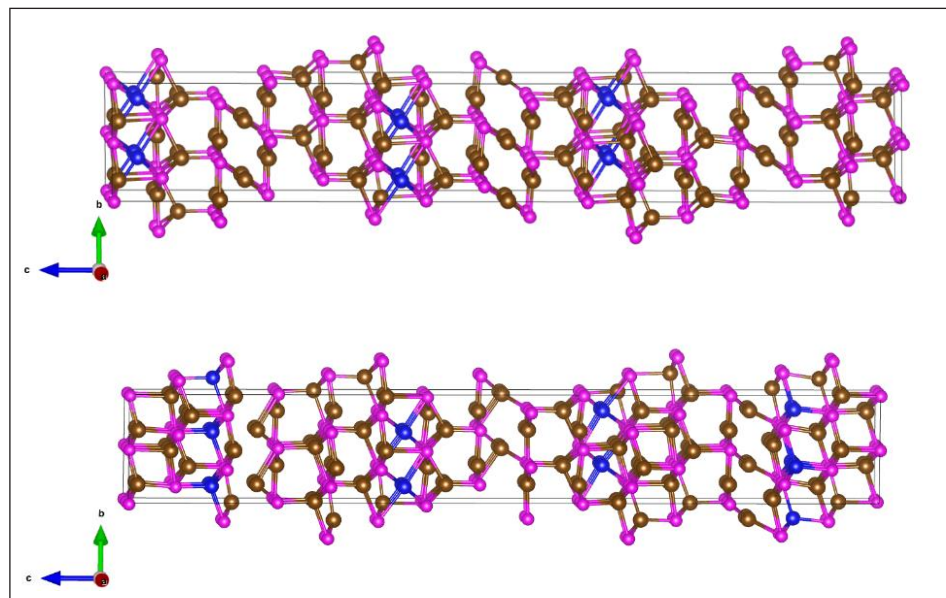


**Figure 3.** *Inclusion of Li (blue sphere) in rhombohedral Cu$_{1.8}$S*

of ~462 mAhg$^{-1}$ and importantly it retains capacity of 240 mAhg$^{-1}$ even after 300 cycles at 0.1 Ag$^{-1}$. In order to rationalize this superior electrochemical performance and good cycling stability, DFT calculations were carried out. Cu$_{1.8}$S has rhombohedral structure with R-3m (No. 166) space group which can also be represented in hexagonal fashion which was used in the DFT calculations. The lattice parameters of the relaxed unit cell of Cu$_{1.8}$S are a=b=3.877 Å, c=46.815 Å; α=β=90$^o$ and γ=120$^o$ which are close to experimental values (a=b=3.93Å, c=48.14Å; α=β=90$^o$ and γ=120$^o$). The structure of Cu$_{1.8}$S is quite different from Cu$_2$S. Whereas, hexagonal Cu$_2$S structure (P6$_3$/mmc -No. 194) does not have Cu atoms in tetra coordination and octahedron (distorted) of six coordinated Cu atoms is continuously connected, on the contrary Cu$_{1.8}$S has multi-size polyhedrons (3,4 and 6) due to fractional stoichiometry of Cu atoms. [3]

This multi-size polyhedron structure offers two major channels for Li ion movement along the a-direction. One of the channels have on one sit 3/6 coordinated Cu and other side tetra-coordinated Cu atoms along c-direction. On the contrary other channel have tetra coordinated Cu atom on either side. DFT calculations were carried out after introducing the Li atoms in the two channels. For both the channels, along the c-direction maximum lattice expansion takes place and in turn provide cushioning via its multi-size polyhedron layers. [3]

Importantly, for expansion in both channels does not leads to formation of any S-S bond.[4] Energetically, inclusion of Li at the six-fold coordination site in the copper tetrahedron layers is preferred. Metal rich nature of Cu$_{1.8}$S

eliminates the closeness of S atoms and hence S-S bond. Further after the lithiation, controlled fashioned swelling of $Cu_{1.8}S$ does not encounter formation of S-S bond and structure sustains during cycling. Thus, DFT successfully rationalize the experimental observation that pristine $Cu_{1.8}S$ anode, even after significantly higher loading ~ 2.8 mg $cm^{-2}$ could be run for 300 cycles (Simultaneous presence of higher cyclability and loading). During lithiation, the structure mediated flexibility of $Cu_{1.8}S$ structure enables the reasonable retention of capacity along with high cyclability.

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**Dr. Sandeep Nigam** *did his M.Sc. from Rajasthan University, Jaipur and later joined Chemistry Division, Bhabha Atomic Research Centre in 2003 after graduating from 46th batch of BARC training School. Since then he has been actively involved in the field of nanomaterials, catalysis, phosphors and cluster science. He was awarded Ph. D. degree from Mumbai University in year 2008 for his theoretical work on pure and mixed clusters. He has worked as a visiting Scientist at Physics Department, Michigan Tech. University, Houghton, USA. He is having - 80 publications in refereed international journal of high repute.*

**Dr. Adish Tyagi** *did his post-graduation in Chemistry from Delhi University, Delhi in 2010 and joined BARC in 2012 after successful completion of one year orientation course from BARC Training School. He obtained his Ph.D. degree in Chemistry from HBNI in 2018. Currently, he is working as Scientific Officer-E in Chemistry Division of BARC. His research interests include synthesis of organometallic molecular precursors for technologically important nanomaterials, development of efficient phosphor for white light emission and purification of strategic materials.*

**Dr. B. P. Mandal** *completed MSc from University of Burdwan, West Bengal in 2003. He was awarded the PhD degree in Chemistry in 2009 by Mumbai University. He did his postdoctoral research in development of new electrodes for Li ion battery at Wayne State University, USA. He was awarded DAE-Young Scientist award in 2012. He has been awarded membership of National Academy of Science, India and also he has received DAE-SSPS Young Achiever Award in 2017. Presently he is involved in development of battery materials. He has transferred the technology for synthesis of electrode materials for lithium ion battery to different Indian companies for commercialization. Dr. Mandal has been awarded with SMC Bronze medal in 2022. Dr Mandal has authored more than 90 scientific papers in the journals of international repute.*

**Dr. Majumder** *joined Chemistry Division, BARC in 1992 after successful completion of BARC training school program. The primary thrust of his research has been in theoretical understanding of materials at different length scale starting from clusters to nanomaterials to extended surfaces. In particular, Dr. Majumder has contributed towards understanding the physico-chemical properties of metal clusters and their applications in the field of catalysis for hydrogen production and storage materials. On the basis of these research work Dr. Majumder has published more than 150 manuscript in International Journals.*

# Chalcogenide based Thermoelectric Material

**Shovit Bhattacharya[1,2,*], Ranu Bhatt[1], Ajay Singh[1,2], Pritam Sarkar[1,2], K.P. Muthe[1]**
*[1]Technical Physics Division, Bhabha Atomic Research Centre, Mumbai -400085*
*[2] Homi Bhabha National Institute, Anushakti Nagar, Mumbai-400094*
*\*shovitb@barc.gov.in*

## Abstract

The ever increasing demand for energy throughout the world along with $CO_2$ emissions has accelerated the search for clean and renewable sources with noble approaches towards efficient energy management. It is found that around 60-70% of energy is lost in the form of heat. In this direction, one of the most promising avenue is the conversion of the waste heat into electricity. The thermoelectric materials can generate electricity from a temperature gradient, thereby recycling the abundant waste heat. These type of devices are known as thermoelectric generators (TEG). Additionally, thermoelectric materials can be used for cooling applications. This can be achieved by passing electric current which in turn creates a temperature gradient, these type of devices are known as peltier coolers. The former is based on the Seebeck effect, and the latter on the Peltier effect. This article will focus on various chalcogenides as thermoelectric materials

## Introduction:

Increased demand for electric power, throughout the world, has fuelled a very important mission to find alternative, renewable and sustainable power sources. This development of alternative power sources will accelerate the transition from the use of fossil fuel to sustainable energy production along with a reduced emissions of carbon dioxide. It is worth mentioning that a considerable amount of the energy produced is lost as heat and only less than half, satisfy the needs of human society. In this respect, as the existing energy sources have been depleting at a fast pace, thermoelectric materials have received significant attention in recent years due to its role in conversion of waste heat into electricity.

Studies on thermoelectric started since early 19th century. The most important discovery in thermoelectric were made between 1821 and 1850 which included the discovery of three thermoelectric effects, namely, Seebeck, Peltier and Thomson effects. (1) Altenkirch analysed the problem of energy conversion using thermocouples, in the year 1911 (2). He showed that the performance of a thermocouple could be improved by increasing the magnitude of the differential Seebeck coefficient (S), by increasing the electrical conductivities (σ) and by reducing their thermal conductivities (κ). Describing the thermoelectric figure of merit.

The thermoelectric (TE) devices have triggered great attention in viable technologies including automotive, military equipment, aerospace, medical and industries. Unlike other devices, they have many advantages, such
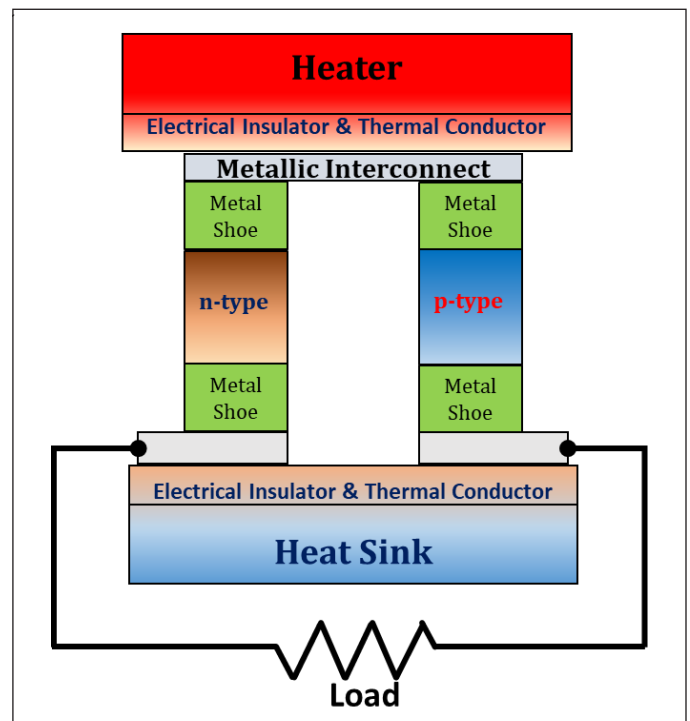


*Figure 1: Schematic of the internal architecture of a single p-n leg based thermoelectric power generator showing different electrical and thermal interfaces*

as, long life, usage without any vibrations or noise due to absence of mechanically moving parts. Furthermore they are compact, possess a high level of scalability, reliability and require minimum maintenance.

Traditional thermoelectric materials were based on the binary tellurides $Bi_2Te_3$ and PbTe, which have been utilized for decades. The focus on tellurium as the heaviest non-

radioactive chalcogenide stems from the observation that heavier elements are advantageous for a reduced thermal conductivity, which is essential for the thermoelectric energy conversion. Moreover, tellurides are less ionic than sulphides or selenides, which leads to an enhanced carrier mobility that is advantageous for the desired high electrical conductivity. This review presents these traditional routes to low thermal conductivity, as well as alternatives based on the lighter analogues of tellurium, namely sulphur and selenium.

Due to the urgency of our energy and environmental issues, a variety of cost effective and pollution-free technologies have attracted considerable attention, among which thermoelectric technology has made enormous progress. Substantial numbers of new thermoelectric materials are created with high figure of merit (ZT) by using advanced nanoscience and nanotechnology. This is especially true in the case of metal-chalcogenide-based materials, which possess both relatively high ZT and low cost among all the different kinds of thermoelectric materials. Here, comprehensive coverage of recent advances in metal chalcogenides and their correlated thermoelectric enhancement mechanisms are provided. Several new strategies are summarized with the hope that they can inspire further enhancement of performance, both in metal chalcogenides and in other materials.

### Layered Chalcogenides:

Layered chalcogenides represent a massive group with multiple materials. In the following section we tried to classify layered materials into groups in which each group has certain common features between the members: (i) bismuth and antimony based materials which are known for their high performance near room temperature; (ii) oxy-chalcogenides; (iii) tin- and indium-based materials (3); (iv) homologous series; (v) layered sulfides, including titanium sulfides; and (vi) ternary $ACrX_2$ layered structures (4). The structure of chalcogenide materials is characterized by layers; the bonds in each layer are strong covalent bonds, which provides in-plane stability. The interaction that holds the layers together is van der Waals. According to the chemical bonding and anisotropic nature of the crystal structure, there is variation in thermoelectric properties with different crystallographic directions within the crystal. Details of the structure of individual material and their thermoelectric properties and discussion of how the anisotropic nature of layered materials affects their thermoelectric properties are presented in the following sections

### Bismuth and Antimony-Based Layered Materials

In this section we include Bi and Sb telluride and selenide materials, whereas sulfides' compounds are excluded and discussed under the sulfide group. Although sulfur lies in the same group as Te and Se, however, bismuth sulphides adopt an orthorhombic structure different than rhombohedral structure adopted by bismuth tellurides and selenides.

Sulfides show lower electrical conductivities compared to selenide and telluride because of their higher bandgap (5; 6; 7)

Bismuth telluride ($Bi_2Te_3$) is a narrow bandgap n-type semiconductor of (0.21 eV) and an indirect bandgap of 0.15 eV. Bismuth telluride has a distinctive rhombohedral layered crystal structure with five atoms in each unit cell forming quintuple layers of Te(1)-Bi-Te(2)-Bi-Te(1) stacked together by weak van der Waals forces along the c-axis as shown in Figure 1 (8) . The Te atoms are presented in two different chemical states as the subscripts 1 and 2 show.
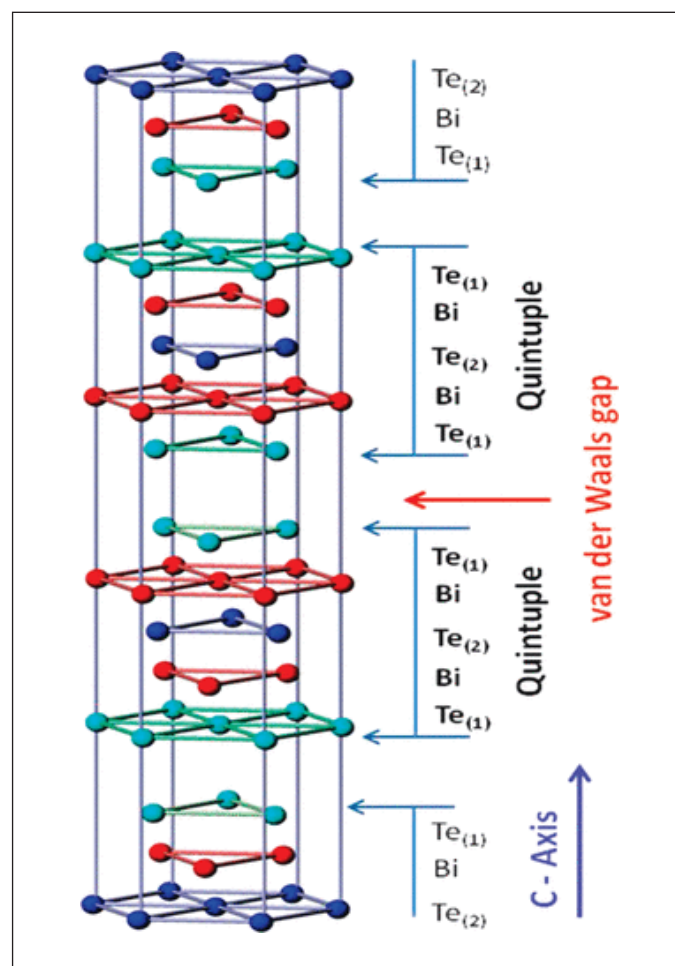


*Figure 2  Crystal structure of Bi2Te3. Reprinted with permission from (8)© {2010} ACS.*

However, within the layers, Bi-Te$_{(2)}$ atoms are bonded by a strong covalent bond, whereas Bi-Te$_{(1)}$ atoms are bonded by a covalent-ionic bond (9).

Since its discovery 60 years ago, bismuth telluride was first used by Goldsmith as an effective material for refrigeration purposes. It has been used as the most promising thermoelectric material with a high figure of merit (1.14) near room temperature (200–400 K) (6). Because of the weak van der Waals bonds between layers, Bi$_2$Te$_3$ exhibits high thermoelectric properties and demonstrates easy cleavage along the (001) plane (9).

Analogues to Bi$_2$Te$_3$, bismuth selenide (Bi$_2$Se$_3$) is also a narrow bandgap (0.3 eV) n-type semiconductor. Analogous to bismuth telluride, it has a rhombohedral anisotropic layered structure with quintuple layers and five atoms in each unit cell (6). The two Bi atoms and three Se atoms are packed similar to Bi$_2$Te$_3$ pattern Se(1)–Bi–Se(2)–Bi–Se(1) with weak van der Waals bonds between neighbouring Se(1) planes. Compared with bismuth telluride, bismuth selenide possesses high thermal conductivity because of the light atomic weight of Se. Therefore, the thermoelectric performance of Bi$_2$Te$_3$ is much better than Bi$_2$Se$_3$ (9).

## Oxychalecognide Materials

Layered oxychalcogenides thermoelectric materials have gained considerable attention due to their intrinsically low thermal conductivity, moderate Seebeck coefficient and tunable electrical conductivity (10).
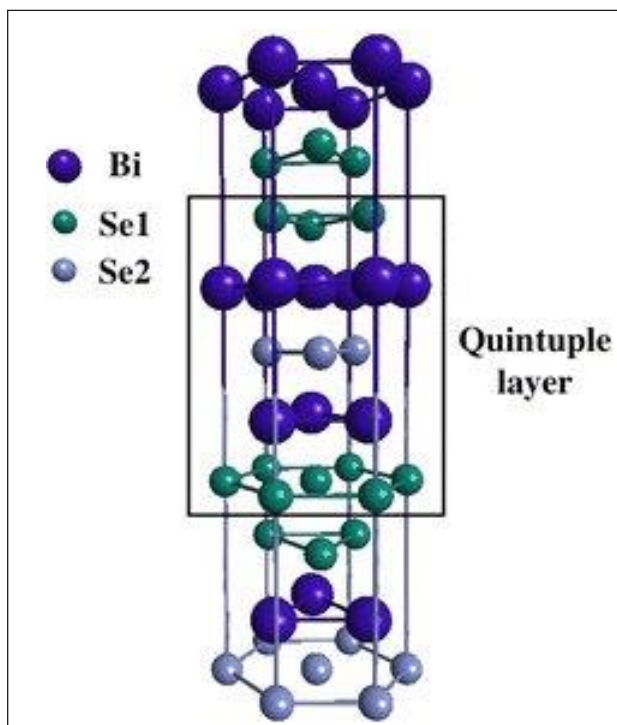


*Figure 3 Crystal Structure of Bi$_2$Se$_3$ (11)*

The Bi-O-X system is a group of oxy-layered materials that has a complex tetragonal structure. One example is Bi2O2Se, which consists of tetragonal (BiO)n layers with Se atoms occupying interlayer positions as shown in Figure 3. Due to the strong electronegativity of oxygen atoms,oxychalcogen systems suffer from low electrical conductivity. However, they exhibit a moderate Seebeck coefficient.

BiCuOCh (Ch = S, Se, Te) is a group of oxychalcogenides that have the structure of space group = P4/nmm and consist of alternately stacked (Bi$_2$O$_2$)$^{+2}$ insulating layers and (Cu$_2$Ch$_2$)$^{-2}$ conducting layers as shown in Figure 4. They exhibit extremely low thermal conductivity and have poor electrical conductivity due to low carrier mobility.
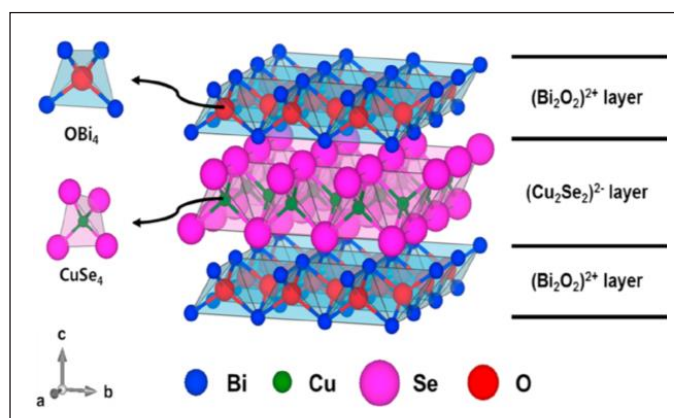


*Figure 4 Crystal Structure of BiCuSeO Reprinted with permission from (12)© {2020} Elsevier B.V.*

BiCuOSe was recently reported as a promising thermoelectric material for its high ZT (> 0.8) at a high-temperature range (923 K). It is a p-type material composed of alternating insulating (Bi2O2)2+ layers with conductive (Cu2Se2)2−. The thermoelectric measurements suggest that the electrical properties of BiCuSe is lower than other thermoelectric systems; thus the high thermoelectric performance of BiCuSe originates from its very low thermal conductivity instead of its power factor (13; 14; 15). Compared with BiCuSeO, BiCuOTe has a higher power factor as it has a better hole mobility attributed to the antibonding between Cu and Te compared with antibonding between Cu and Se. Therefore hole mobility can be improved significantly in BiCuSeTe compared with BiCuSeO (13)

## Homologous Series

Homologous layered materials are an interesting class of thermoelectric materials that are built on the same structure of a certain model and can be expanded by regular increments in different directions (16) (3) (17)

(18) (19). Examples of homologous thermoelectric series are $CsBi_4Te_6$, a member of the $Cs_4[Bi_{2n+4}Te_{3n+6}]$ homologous series, and $Pb_5Bi_6Se_{14}$, a member of the cannizzarite homologous series.

$CsBi_4Te_6$ is a p-type semiconductor with a narrow bandgap of (0.1 eV), which is nearly half the value compared with $Bi_2Te_3$. It has an anisotropic layered structure with Bi4Te6 slabs interconnected by Bi-Bi bonds parallel to the b-axis and altered with Cs+ ionic layers as shown in Figure 5. $CsBi_4Te_6$ is a potential candidate for thermoelectric application and exhibits a high figure of merit of 0.8 at low temperatures, which is attributed mainly to the narrow bandgap (16) (6) (20)
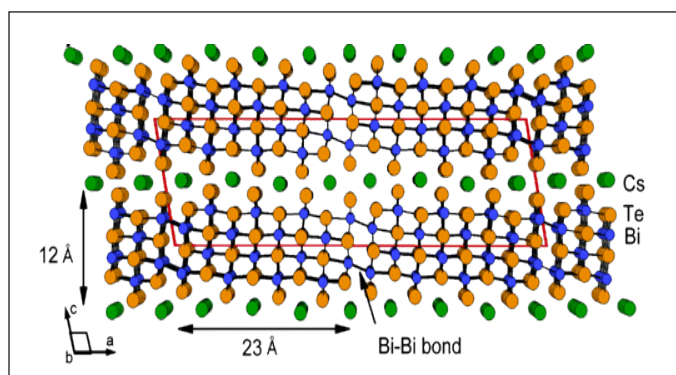


**Figure 5** *Crystal structure of $CsBi_4Te_6$ along the b-axis Reprinted with permission from (20) © {2004} ACS.*

$Pb_5Bi_6Se_{14}$ is an n-type semiconductor. Its crystal structure consists of infinite alternating PbSe- and $Bi_2Se_3$-type layers along the c-axis, forming a three-dimensional structure, as shown in Figure 6 (21). The interfaces between
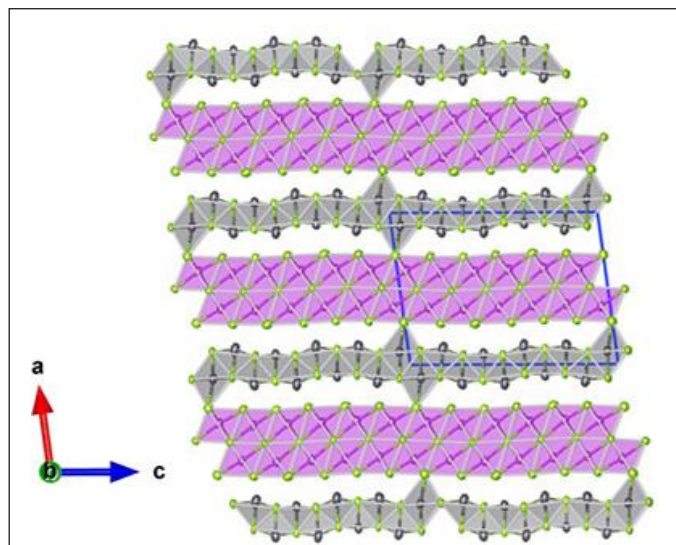


**Figure 6** *Crystal structure of $Pb_5Bi_6Se_{14}$ along the b-axis Reprinted with permission from (21). © {2018} ACS*

the PbSe and $Bi_2Se_3$ layers scatter phonons as well as charge carriers, leading to a highly anisotropic electrical mobility and lattice thermal conductivity between in- and cross-plane directions. Electrical conductivity is much higher in-plane direction than cross-plane direction, whereas lattice thermal conductivity is slightly higher for the in-plane direction than for the cross-plane direction.

However, the Seebeck coefficient is insensitive to the crystal orientation and exhibits nearly similar values for both in- and cross-plane directions. As a result, a higher ZT of 0.46 has been achieved for the in-plane direction at 75 K. The thermoelectric properties of homologous compounds can be controlled by modifying the shape and size of the structural module. Therefore, homologous materials are a suitable platform for developing new thermoelectric materials (16)

## Sn- and In-Based Materials

Tin selenide (SnSe) is a p-type semiconductor with simple orthorhombic, layered structure material with a zig-zag chain along the b-axis with a bandgap of 0.86 eV. Each layer consists of two-atom-thick slabs (Se and Sn) along the in-plane direction, with strong Sn-Se bonds within the layer and weak Sn-Se bonds between layers along the cross-plane direction, as shown in Figure 7.
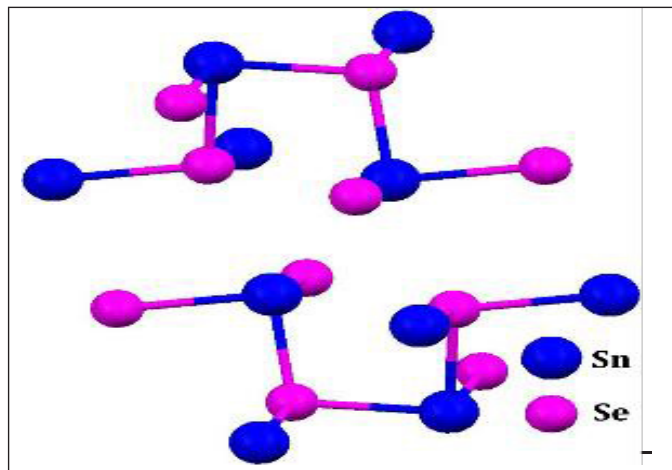


**Figure 7** *Crystal structure of SnSe*

At 800 K, tin selenide undergoes reversible transition distortion from the orthorhombic low temperature *Pnma* space group to the orthorhombic high temperature *Cmcm* space group. At this transition temperature, the power factor reaches its maximum value as the *Cmcm* phase exhibits a reduction in energy with enhancement in carrier mobility while preserving the low thermal conductivity (22)-(23) Similarly, $In_4Se_3$ forms a layered crystal structure of $(In_3)^{+5}$ clusters covalently bonded to Se ions in the in-

plane. Along the cross-plane direction, the-planes are held together by van der Waals interactions as shown in Figure 8. Tin selenide is a p-type semiconductor with a relatively low carrier density of $10^{17}$–$10^{18}$ cm$^{-3}$.



*Figure 8 Crystal structure of In$_4$Se$_3$ Reprinted with permission from (24) © {2022} The Chinese Ceramic Society. Production and hosting by Elsevier B.V.*

It possesses a high electrical resistivity of 10–10$^5$ cm at ambient temperature. Its power factor is moderate at high temperatures as the crystals possess a high Seebeck coefficient and are much higher than other materials with low intrinsic thermal conductivity (23). SnTe was generally ignored owing to its relatively low electrical conductivity, until Sassi, S, et. al. reported a high ZT of 2.6 for a single crystal along the b-axis, 2.3 along the c-axis, and 0.8 along cross the plane direction (a-axis) (22).

The p-type SnS is isostructural to SnSe with the added advantage of being environmentally friendly and earth abundant, thereby cost effective. The SnS has extremely low thermal conductivity (below 1 Wm$^{-1}$K$^{-1}$) with a high Seebeck coefficient, which makes it a promising material for thermoelectric application (25).

The Figure 9 represents ZT of various Chalcogenide based thermoelectric materials.

**Other Layered Materials**

Various other materials with layered structure, have been identified as excellent thermoelectric materials due to the fact that there is a separation of charge carriers and phonons owing to the layer structure. The charge carriers can be effectively transferred within the layers and at the same time phonons can be scattered due to the weak van der Waal bonding between the adjacent layers. The layered structure materials in this group are mainly transition metal chalcogenides (such as TiS$_2$, MoSe$_2$, ZrSe$_2$, MoS$_2$, WSe$_2$, etc.), and ternary ACrX$_2$ materials, in which A is Cu, Ag, or Ni. These compounds display phonon liquid electron

crystal (PLEC)" property (26), which is very similar to the concept of "phonon glass electron crystal (PGEC)". The PLEC compounds usually are superionic materials. In these materials the chalcogen anions form a crystalline lattice and provide pathways for the charge carriers, while the Cu/Ag cations are highly disordered around the chalcogen, as shown in Figure 10. The Cu/Ag ions can move fast and behave like a liquid at high temperature, which leads to their extremely low thermal conductivity while preserving good electrical conductivity. Due to these complementary effects these materials show wonderful ZT values. Materials like AgCrSe$_2$ and CuCrSe$_2$ have shown ZT values near 1, however Bhattacharya et.al. (26) could enhance the ZT to 1.4 by mixing AgCrSe$_2$ and CuCrSe$_2$

In addition there are Misfit layered sulfides which are large group of layered material with a general formula [MS]$_{1+m}$[TS$_2$]$_n$, where M=Sn, Pb, Sb, Bi, or rare-earth metals; T = Ti, V, Cr, Nb, and Ta; and n = 1, 2, 3 (27) and 0.08<m<0.28. These materials consist of alternating layers of MS and TS$_2$ where the TS$_2$ layer provides the electron path way and thermopower whereas the intercalated MS layer suppresses the transport of phonons. The crystal structure and physical properties of this misfit family were studied extensively during the ninties, however, not many reports on their thermoelectric properties exist till date.



*Figure 9: Crystal structure of CuCrSe2*

The figure 10 is a representative graph of ZT values of various chalcogenides

The table 1 shows a compilation of various Chalcogenide based materials along with their ZT values.

**Table 1: Layered chalcogenide materials with their ZT values**

| Material | Type | ZT | T,K | Reference |
|---|---|---|---|---|
| $Bi_2Te_3$ | n | 0.4 | 300 | (28) |
| $Bi_2Se_3$ | n | 0.75 | 423 | (29) |
| $Ti_{1.008}S_2$ | n | 0.12 | 300 | (30) |
| $Cu_{0.1}TiS_2$ | n | 0.5 | 800 | (31) |
| $(BiS)_{1.2}(TiS_2)_2$ | n | 0.28 | 700 | (32) |
| $(BiS)_{1.2}(TiS2)_2$ | n | 0.24 | 750 | (33) |
| $(SnS)_{1.2}(TiS_2)_2$ | n | 0.37 | 700 | (33) |
| $(PbS)_{1.18}(TiS_2)_2$ | n | 0.28 | 700 | (33) |
| $(Yb_2S_2)_{0.62}NbS_2$ | p | 0.1 | 300 | (34) |
| $Bi_2S_3$ | n | 0.08 | 773 | (35) |
| $Pb_5Bi_6Se_{14}$ | n | 0.01 | 300 | (36) |
| $Pb_5Bi_{12}Se_{23}$ | n | 0.01 | 300 | (36) |
| $Pb_5Bi_{18}Se_{32}$ | n | 0.03 | 300 | (36) |
| SnSe (single crystal) | p | 2.62 (b-axis) | 923 | (37) |
| SnSe (bulk) | p | 3.1 | 783 | (38) |
| SnS | p | 0.41 | 848 | (25) |
| InSe | n | 0.525 | 600 | (39) |
| $In_4Se_3$ | n | 0.6 | 700 | (40) |
| $AgCrSe_2$ | p | 0.81 | 773 | (26) |
| $CuCrS_2$ | p | 0.9 | 350 | (41) |
| $CuCrSe_2$ | p | 0.95 | 773 | (42) |
| $(AgCrSe_2)_{0.5}(CuCrSe_2)_{0.5}$ | p | 1.4 | 773 | (26) |
| $NiCr_2S_4$ | n | 0.024 | 313 | (43) |
| $Bi_2O_2Se$ | n | 0.2 | 800 | (44) |
| $Bi_4O_4S_3$ | n | 0.03 | 300 | (45) |
| $Bi_{1.9}O_2Se$ | n | 0.12 | 773 | (46) |
| BiCuSeO | p | 0.5 | 650 | (47) |
| $BiCu_{0.975}SeO$ | p | 0.81 | 650 | (47) |
| BiCuOTe | p | 0.51 | 600 | (48) |
| BiCuOS | p | 0.07 | 650 | (49) |
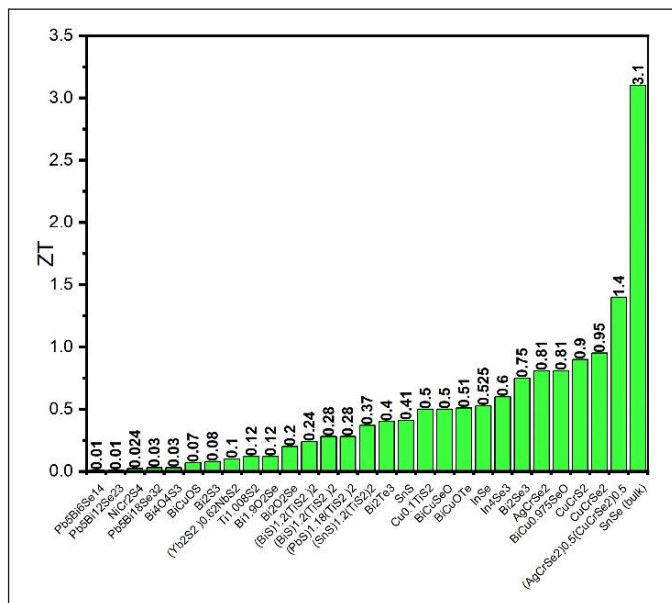


***Figure 10:*** *ZT of various chalcogenide based TE materials*

**Summary**

In this article we have tried to present an overview of the properties and structure of chalcogenides as thermoelectric material, as they possess various structures with different compositions and relatively low fabrication costs, offer a good platform for either searching for new thermoelectric materials or discovering new theories that can lead to high thermoelectric performance. Significant advances in improving the thermoelectric performance of chalcogenide based materials have been made in the last few decades.

We have also tried to briefly describe the current directions in which the research on chalcogenide based thermoelectric material is being perused. In this article we have clubbed the most studied chalcogenide based material upon the share of its publications. Based on which it can be inferred that traditional Bi–Te/Se and Pb–Te systems would continue dominate the commercial market because of their mature processing technologies along with better performance as compared to other chalcogenides. However, more effort needs to be channelized towards enhancing their mechanical strength and reducing fabricating cost.

Low dimensional metal sulphides and selenides would attract considerable attention due to the possibility of simultaneous optimization of the thermal and electrical conductivity via separating the transfer of charge carriers from that of phonons, and their lower cost, environmental friendliness, as well as simple composition. Also, the stable PLEC materials with high performance would be a focus for future research

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**Dr. S. Bhattacharya** *joined Bhabha Atomic Research Centre as Dr. KS Krishnan Research Associate in 2003 after completing his PhD in Physics from Barkatullah University, Bhopal. At present he is working as a Scientific Officer (F) at BARC. His present interests include development of high performance thermoelectric materials and fabrication of thermoelectric device, development of nano-materials for various applications like hydrogen gas sensor for area monitoring.*

**Dr. Ranu Bhatt** *joined Bhabha Atomic Research Centre, Mumbai in 2010 as Dr. K.S. Krishnan Research Associate and presently working as Scientific Officer. After obtaining her Ph.D. in 2008 from UGC-DAE Consortium for Scientific Research, Indore Centre, she worked as a Post-Doctoral Fellow at Max-Planck-Institut for Intelligent Systems, Stuttgart, Germany. Her current research focuses on the investigation of advance thermoelectric material and development of thermoelectric devices.*

**Dr. Ajay Singh** *is presently working as Scientific Officer (H) at Technical Physics Division of Bhabha Atomic Research Centre (B.A.R.C.). He joined B.A.R.C. in 1999 after passing through 42nd Batch of B.A.R.C. Training School. His present research interest includes design and development of high performance thermoelectric materials, thermoelectric power generators and associated electrical circuits for practical applications.*

**Dr. K.P. Muthe** *is currently heading the Thin Film Devices Section of Technical Physics Division. He joined BARC through the 30th Batch of Training School in 1987. His present field of interest are: development of has sensors, hydrogen mitigation, thermoelectric generators and radiation dosimetry.*

**Mr. Pritam Sarkar** *did his Masters in Physics, from Jadhavpur University and joined Bhabha Atomic research Centre, through the 59th Batch of Training School. Subsequently he joined Technical Physics Division in 2016. At present he is working as a Scientific Officer (D) and his field interest are: Synthesis and characterization of Silicides based bulk thermoelectric materials, thin film inorganic and organic thermoelectric materials for waste heat power generation.*

# Bottom-up synthetic approaches towards nanostructured metal chalcogenide materials: technologically important class of compound semiconductors

**Gourab Karmakar**

*Chemistry Division, Bhabha Atomic Research Centre, Mumbai- 400 085*
*Email: gourabk@barc.gov.in*

## Abstract

Depleting fossil fuel reserve and raising environmental concerns in the present time necessitates scientific exploration of environmentally clean energy resources and storage materials. In this aspect, metal chalcogenides in their nano-domain or in thin film form have emerged as multi-functional materials which found extensive application in photovoltaic and thermoelectric devices as well as in alkali ion batteries, memory devices, supercapacitors and whatnot. This article focuses on the basic principles of various synthetic routes that has been explored to synthesize these auspicious materials over the years. This account will highlight the role of solvent, precursor, reaction time, temperature and several other factors in detail which can lead to tailor made metal chalcogenide nanomaterials and thin films in terms of size, morphology, optical band gap etc. Some recently reported synthetic procedures along with the modification have also been included here. The author believe that, this article will serve as a useful account to researchers for the exploration of various synthetic routes to metal chalcogenides nanostructures as potential energy conversion and storage materials.

## Introduction

Unrestricted utilization of fossil fuel reserve of earth to cater the ever-growing energy demand of mankind results in severe ecological problems and have been considered as an issue of global importance [1]. It is believed by the scientific fraternity that the future energy needs will be served by the renewable sources rather than fossil fuel. This phenomenon require the development of economic, efficient and environmentally friendly energy conversion and storage (ECS) devices that can fulfil the energy need of the future generation. Typical ECS devices include fuel cells, solar cells, photoelectrochemical water splitting cells, alkali ion batteries (Li and Na-ion batteries or LIBs and SIBs), supercapacitors, thermoelectric (TE) and memory devices [2]. Their performance is solely dependent on the properties of the active material, mostly in nano-form, present in these devices. Constant research towards new developments in the field of nano-science are the need of the hour to develop efficient ECS devices [3].

Among several materials tested for various ECS devices, metal chalcogenides (MCs) nanomaterials, in particular, have been considered as one of the best performers. They are the material of choice for a variety of energy applications which includes LEDs, fuel cells, solar cells, sensors, LIBs and SIBs, supercapacitors, thermoelectric and memory devices [4]. The distinct properties of the MCs, which make them particularly

interesting are, high power density, high molar absorption coefficient (upto $10^5$ cm$^{-1}$), high specific capacitance, flexible operating temperature, band gap tunability along with earth abundant, economic and environmentally benign nature. In addition, nanostructured MCs provide a number of ways by virtue of which, their physical and chemical properties can be engineered to meet the demands and future challenges of energy conversion and storage (Fig. 1) [5]. These abovementioned physical and chemical properties of MCs are also a function of the size and morphology of the nanostructures, which leads the discussion to the synthetic methods for these exotic materials and their nanostructures. Synthetic process adopted for the MC nanostructures are of paramount importance because with proper choice of synthetic route and conditions; size, morphology and properties of the MCs can be rationally tuned to requirement [6].

Synthesizing nanostructured MCs in phase pure form is of prime importance for the ECS industries. It is also important to realize that Single-component MC nanomaterials may not be able to fulfil the stringent requirements of future ECS devices in terms of their intrinsic physical properties like absorption coefficient, conductivity, seebeck coefficient and thermal stability. For this reason, additional improvement by means of introducing one or more different materials (carbonaceous, metallic, metal oxide or different chalcogenide materials)
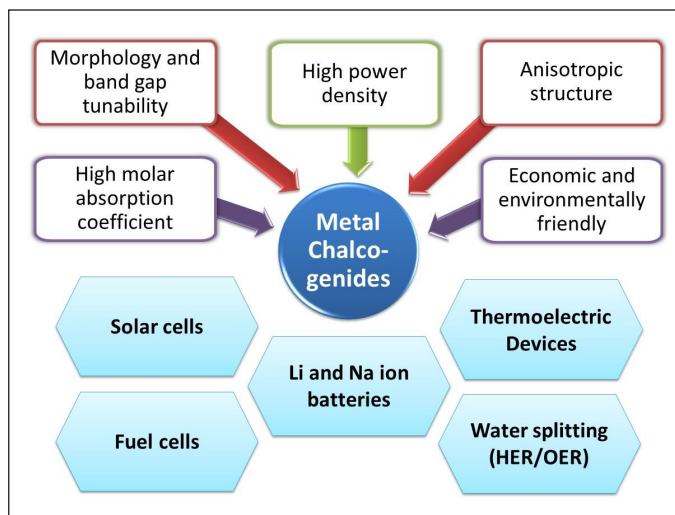
**Fig. 1.** *Schematic illustration of properties and potential application of metal chalcogenides in energy conversion and storage devices.*

with MC nanomaterials to synthesize of heterostructure or composites have also been studied which allows scientists to impart desired properties into the MCs [1].

This article aims to provide a basic understanding of the intriguing chemistry behind the synthetic strategies for MC nanomaterials. Both the solvent assisted and solvent less routes have been discussed. To elaborate, we start this article with an overview of broad classification of the synthetic routes. Then the recently emerging bottom-up approaches or the chemical routes to MC nanomaterials are presented in a detailed fashion followed by the opportunities and major challenges associated with the MC nanostructure synthesis.

## Synthetic strategies for MC nanostructures and thin films

Innovative synthetic protocols for device worthy MC nanomaterials and thin films which can be scaled to large quantity with control over morphology, size, composition and structure is highly desirable. There are only two fundamental synthetic routes to achieve nano-sized material (Fig. 2). These are top-down or physical approach and the bottom-up or chemical approach. The top-down pathway involves slicing down any bulk material by controlled mechanical technique to bring down to nanoscale [7]. These include ball milling, laser ablation, sputtering techniques etc. The bottom-up approach is the reverse of top-down approach. It involves synthesizing nanomaterial by joining atom by atom, molecule by molecule, cluster by cluster (self-organization process). In this mode, self-assembled features of single atoms or molecules are exploited to construct complex structures and morphologies at the nano-regime.

The bottom-up technique are classified into two categories based on the involvement of solvent/capping agent/surfactants. These are solvent-assisted and solvent-free synthesis. Both the methods have their own advantages and disadvantages. In a solvent mediated synthesis, the employed precursors and/or surfactants can be calculatedly adjusted based on the target MCs nanostructures. It also allows control over nucleation and growth process by rational alteration of the thermodynamic and kinetic parameters such as temperature, time of the reaction which may lead to tailor made characteristics. However, involvement of organic solvents and sophisticated apparatus restricts the scalability of this technique. Solvent less synthesis, on the contrary, though scalable, suffers from the fact that is uses high temperature and pressure conditions and allows less control over the phase, stoichiometry, morphology and optical properties of the MC nanomaterials.
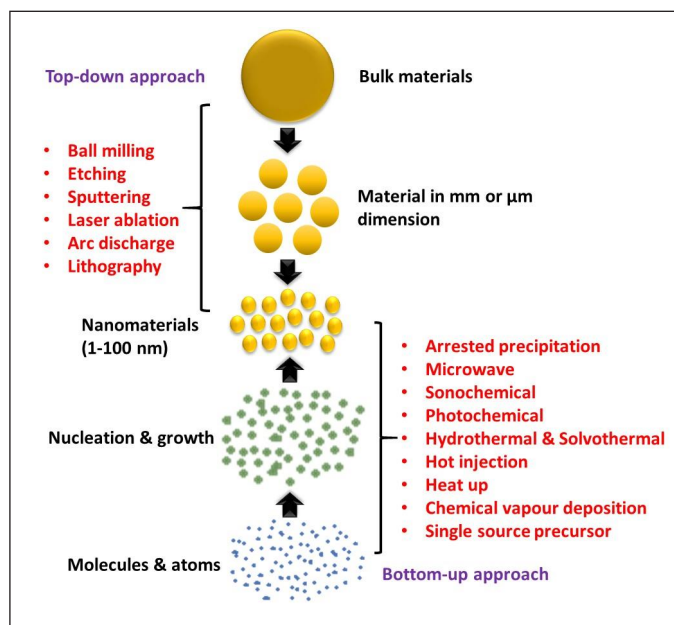


**Fig. 2.** *Schematic diagram for different approaches for MC nanomaterials synthesis.*

## Synthesis of MC nanostructures

### Arrested precipitation method:

Some of the very first examples of nanomaterials synthesis through chemical route made use of this method. Controlled precipitation of metal sulfide nanomaterials was demonstrated from dilute sulfide solutions by rapid termination of growth and nucleation. For instance, Brus et al. have achieved the synthesis of CdS nanoparticles by adding a $(NH_4)_2S$ solution to a $CdSO_4$ solution in a controlled fashion followed by arresting the reaction by an

increase in pH [8]. In this approach, control over the growth of nanoparticles can be achieved through proper choice of solvent, pH and stabilizer or capping agent.

**Solid-state pyrolysis:**

Solid state pyrolysis is the simplest approach towards MC materials which doesn't involve multiple steps, organic solvents or even capping agents. It is a single-step decomposition reaction where the molecular precursor is heated in a boat (quartz/alumina/glass) under inert atmosphere or in air to produce the final material. This method attracted limited popularity because of lack of versatility. Absence of capping agents makes it difficult to isolate nano-sized particles. Tuning size, morphology, composition and optical properties also becomes difficult due to less control over the kinetics of decomposition. Moreover, due to the volatile nature of S/Se, this method often ends up giving chalcogen deficient materials [9]. This strategy has been successfully utilized for the synthesis of various thermoelectric materials.

A modified version of straight forward pyrolysis reaction, known as melt-decomposition method has been developed. In this method, reactive melts of reactants (metal and chalcogen precursors) are first generated through controlled heating followed by mixing the melts to a homogeneous one. Then the temperature is raised to initiate decomposition which finally yields MC nanomaterials [10]. Melt decomposition is assisted by the "self-capping" process, which means that the ligands produced during the precursor's decomposition can cap the nanoparticles. For example, O'Brien and co-workers have synthesized CdS nanoparticles by the decomposition of the complex [Cd{$S_2$CNMe($C_{18}H_{37}$)}$_2$] at varied temperatures between 150-300°C [11].

**Hot-Injection method:**

In hot injection method, precursor solution/suspension containing the constituent atoms for the desired nanostructures is swiftly injected in pre-heated high boiling coordinating solvents. This method is quite popular for the production of high-quality monodispersed nanoparticles of metals, semiconductor MCs, metal oxides along with composites of MCs with uniform size distribution. The key factor which make this method quite useful is well separated nucleation and growth [1]. Short burst of nucleation is triggered when suitable precursor mixtures are rapidly injected into high boiling hot organic solvents, which allows the growth process of nanoparticles to occur at a relatively lower temperature. Bawendi's group first developed this methodology for the synthesis of monodispersed CdE (E = S, Se and Te) nanocrystals [12],

scientists have exploited this method for the synthesis of several transition and non-transition MCs. These include binary $Ag_2E$ (E = S, Se, Te), $Cu_2S$, $FeSe_x$, ZnS, $In_2Se_3$, GeTe, SnSe, $SnSe_2$, $Bi_2Te_3$, $Sb_2S_3$, ternary $CuInSe_2$ etc. Morphology ranging from nanoparticles, nanospheres to nanorods and nanoplatelets can be effectively synthesized by this method. Moreover, the size, morphology, optical band gap of a specific MC can be effectively manipulated by minute alteration in the experimental conditions, such as the type and ratios of the starting reagents, temperature, duration and aging period. For instance.

**Heat-Up method:**

The heat-up method (also known as the "non-injection" method) is an alternative approach to synthesize high quality MC nanocrystals which was developed to bypass the scalability issues of hot-injection method [10]. In this method, the precursors or the reactants are steadily heated from room temperature up to a desired temperature in a suitable solvent under inert atmosphere to form the product (Fig. 3). Thus, this method becomes more facile than the hot-injection one as nanocrystals can be produced in one-pot without the involvement of injection step. The underlying mechanism of nanoparticle production in the heat-up method is similar to that for hot-injection method. The heating process eventually bring about the nucleation of the individual crystallites which grows into mature nanocrystals. However, control over the reactivity of the precursors is necessary to allow homogenous nucleation, which is the key to the formation of monodispersed nanoparticles. This method has been successfully utilized for the synthesis of several high-quality MC nanomaterials ranging from binary to quaternary materials such as $Cu_{1.8}Se$, CdSe, $In_2Se_3$, SnS, $Sb_2S_3$, $CuInSe_2$ and $Cu_2ZnSnSe_4$ (CZTSe). Sarkar et al. demonstrated the synthesis of phase pure $In_2S_3$ nanostructures by heating up a mixture of $InCl_3 \cdot 4H_2O$ and thiourea in oleylamine at 215°C [13]. A variation in reaction duration from 4 to 90 minutes resulted in a gradual morphology transition from wrinkled nanosheets to hexagonal nano discs. They have also established the mechanism of the morphology variation and proved that the nanodiscs are forming via folding and tearing of the intermediate sheets. This is one of the many examples where the heat-up method was used to achieve control over the size, morphology. Thus, it allows physical properties like optical band gap tuning in the MC nanomaterials.

**Hydrothermal method:**

The hydrothermal process uses water as the reaction medium and the reaction is carried out in sealed steel autoclaves with teflon liners well above the boiling point
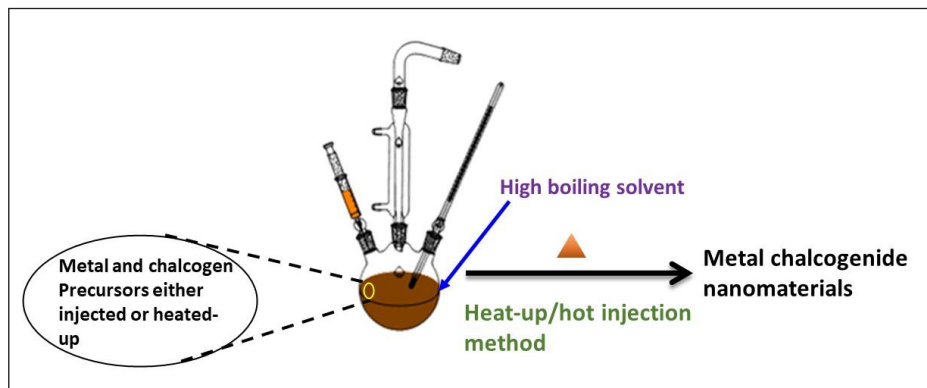
**Fig. 3.** *Schematic diagram for hot injection and heat-up methods for MC nanomaterials synthesis.*
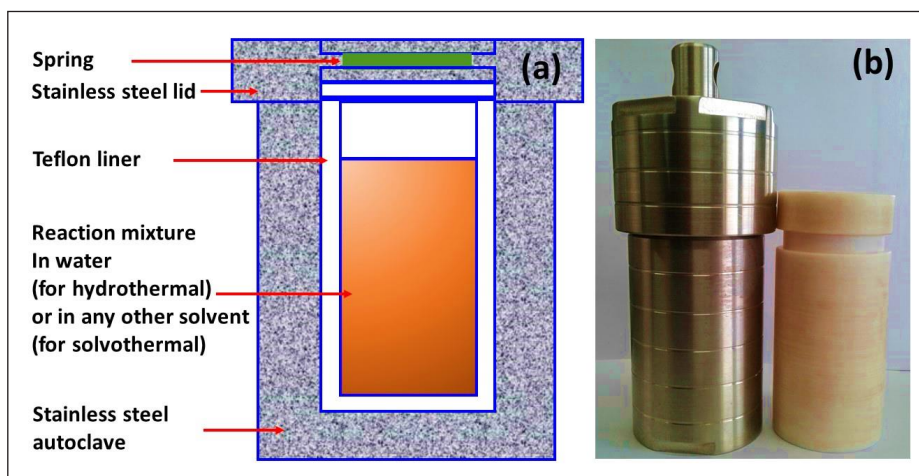


**Fig. 4.** *(a) schematic diagram and (b) actual picture of a Teflon lined stainless steel autoclave used for hydrothermal or solvothermal synthesis of MC nanomaterials.*

morphology of the material to a great extent [14]. Nanowire, Nanotube and nanovesicle-like aggregates have been synthesized with the addition of triethylenediamine, tramethylethylenediamine and di-n-butylamine as linking agents respectively. Other important factors that decide the quality of the final product are monomer concentration and pH of the reaction mixture. An appropriate pH value can affect the hydrolyzation rate of inorganic salts and chalcogen sources, while the monomer concentration controls the morphology of the final product. By carefully these factors along with the reaction temperature and reaction time, MC nanoparticles with tailor made morphology and physical and optical properties can be synthesized.

**Solvothermal method:**

The basic principle of solvothermal method is similar to that of hydrothermal method with the fundamental difference that water is replaced by other organic solvents with varied boiling points, polarity, viscosity etc. Thus, more solvent option can be considered and depending upon the different physicochemical properties of different solvents, reaction temperature and the pressure can also be tuned. With proper choice of solvent, temperature up to 250°C and relatively high pressure than hydrothermal method can be reached. By this method, several MC nanomaterials with an elegant control over size and shape distributions the crystallinity have been synthesized. Typically, elemental chalcogens in powder form (S, Se and Te), thio- or seleno-urea, $Na_2SeO_3$, $Na_2TeO_3$ etc. are used as chalcogen source in this route. Apart from the usual effect of temperature and reaction duration, the nature of solvent also decides the morphology and size. Solvothermal method have been utilized for the synthesis of $Fe_{1-x}S(en)_{0.5}$, $FeS_2$, $Cu_2Te$, $Ag_2Te$ and $Bi_2S$ nanowires; MnSe and MnS nanorods; ZnSe and $Bi_2S_3$ nanobelts; $FeSe_2$, $In_2Se_3$ and $CoS_{1.097}$ nanoflowers; $Cu_{2-x}Se$ and $Cu_2S$ nanodendrites; $Sb_2Te_3$ and CuS nanoplatelets; $In_2S_3$ and $Bi_2S_3$ nanospheres; $FeS_2$ nanowebs, CoTe nanotubes [1]. Synthesis of highly complex concaved cuboctahedrons of copper sulfide nanoparticles is another example of solvent dependent unusual morphology creation by this

of water. Calculated quantity of reactants or precursors are either dissolved or dispersed in water (Fig. 4). The mixture is then transferred and sealed into the autoclave which is then heated to a desired temperature to obtain variety of functional nanomaterials including MCs. Temperature higher than 100°C is used to develop autogenous pressure in the closed system. The in situ generated pressure within the reactor and the heat helps in producing the final MC nanomaterials. This method has been successfully used in synthesizing phase pure MC nanomaterials with exciting morphologies and properties. For instance, NiSe nanowires, nanobelts of $Sb_2E_3$ (E = S, Se and Te), $MoS_2$ hollow cubic cages and $Ag_2Te$ nanotubes and nanoparticles are few of the diverse examples which can be conveniently prepared by this method [1]. Though this method is an aqueous one, small amount of organic ligands are often added to impart tailor made size, shape and properties of MC nanomaterials. For example, copper sulfide nanoparticles can be prepared via this method using CuCl and thiourea. Lu et al. have found out that minute amount of certain organic ligands or linking agents can alter the

route. This is achieved by the use of ethylene glycol media at 140ºC. Each caved cuboctahedron has four identical-hexagonal flakes and contains 14 concave cavities giving rise to a geometrical "stars" appearance. It was found that the use ethylene glycol is the key factor here [15]. Wu and co-workers reported a solvothermal synthetic approach to mesostructured wurtzite ZnS-nanowire/amine nanocomposites with remarkable quantum size effects. This was achieved by using different organic amines such as n-butylamine, ethylamine and tetraethylenepentamine, as solvents. The plausible mechanism of shape-controlled synthesis was attributed to the fact that the amine ligands prefer to attach to the zinc atoms of the (002) face, resulting in the ZnS nanocrystals growing along the c-axis, finally resulting into 1D nanowires [16].

**Microwave method:**

Microwave chemistry was also explored for the liquid phase preparation of various metallic and inorganic nanoparticles including MCs due to its specific advantages such as low costs, less by-product formation and high reaction rate. In microwave synthesis, the reaction proceeds in a fast pace with efficient heating of precursor solution with electromagnetic radiation in the frequency range of 0.3 to 2.45 GHz. The heating of the solution mixture occurs via dipolar polarization and ionic conduction processes [1]. In this route, the size, shape and properties of the final material is a function of microwave dose or reaction time. For instance, Mehta and co-workers have reported a rapid and scalable synthesis of 1D $Sb_2Se_3$ nanostructures by utilizing microwave method [17]. It was found that the morphology of the resulted material can be tuned by changing the microwave dose (power x time). By increasing the dose, a transition from nanowires to nanotubes was obtained. Stucky and co-workers have adopted an ionic liquid assisted microwave route and established it as a general approach for the synthesis of a large number of MC nanomaterials including $Cu_{2-x}Se$, PbSe, PbTe, $Sb_2Se_3$, $Sb_2S_3$, $Bi_2S_3$ and $Bi_2Se_3$ [1].

**Sonochemical method:**

Ultrasound has been a useful tool to chemists for several decades. It has been extensively used to synthesize novel materials with unusual properties, because this method results in particle with small size and high surface area. When solutions are exposed to high ultrasound radiation, bubbles are implosively collapsed by acoustic field. High temperature and pressure fields are produced at the centre of the bubbles. The temperature is estimated to be roughly 5000 K and the pressure crosses 1800 atm, while the cooling rate reaches $10^{10}$ $Ks^{-1}$ [18]. These phenomena cause many chemical reactions to occur. This method offers rapid reaction rate while providing enough control to prepare nanomaterials with uniform size distribution, shape and purity.

Sonochemical method have been used by several groups to prepare technologically important MC nanocrystals. For example, nickel sulfide nanocrystals can be synthesized by ultrasonic treatment of a aqueous solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ in presence of a sulfur source. Thioacetamide, thiourea and sodium thiosulfate pentahydrate can be used as the chalcogen precursor. Similarly, cobalt sulfide nanostructures can also be prepared by using $Co(CH_3COO)_2 \cdot 2H_2O$ in place of nickel acetate. $Bi_2S_3$ nanorods have been successfully synthesized by Wang et al.. Ultrasound treatment of a solution of bismuth nitrate and sodium thiosulfate in presence of EDTA, triethanol amine and sodium tartrate resulted into the desired nanostructures [19]. Liu et al. have reported the synthesis of $Bi_2Se_3$ nanobelts by ultrasonically treating a solution of $H_2SeO_3$ and $BiCl_3$ in presence of hydrazine hydrate. Different reaction time was explored to isolate nanobelts with widths of 20–80 nm and lengths of few micrometers [20].

**Photochemical method:**

Photochemical synthesis depends on the utilization of the power of light sources to induce the decomposition of a certain precursor and then the initiation of the nucleation and growth of the nanocrystals. Various light sources such as LASER, LED, UV and g-ray are often used depending upon the energy needed for synthesis. The photochemical method has been well adopted to synthesize different MC nanomaterials including $Bi_2Se_3$, ZnS, PdS, BiSe, NiS, $WS_2$, $Ag_2Se$ etc. [1]. O'Brien and co-workers have claimed that EuS nanocrystals with a diameter of 9 nm can be isolated by the photolysis of $Na[Eu(S_2CEt_2)_4] \cdot 3.5H_2O$ as a precursor shining white LED light at room temperature [21]. In comparison with other synthetic methods, this photochemical strategy is environmentally friendly and is economic, safe and operates at low temperature or even room temperature. However, this method face issues from scale-up point of view.

**Single source molecular precursor method (SSP):**

A single source precursor is necessarily an organometallic or metal-organic complex which contains all the constituent atoms of the desired material in a covalently bonded fashion. Thus, a SSP for metal chalcogenide must contain both the metal and the chalcogen and there should be a physical bond between them. These SSPs, when decomposed under certain temperature, yield metal chalcogenides directly. It is also to be noted that a SSP
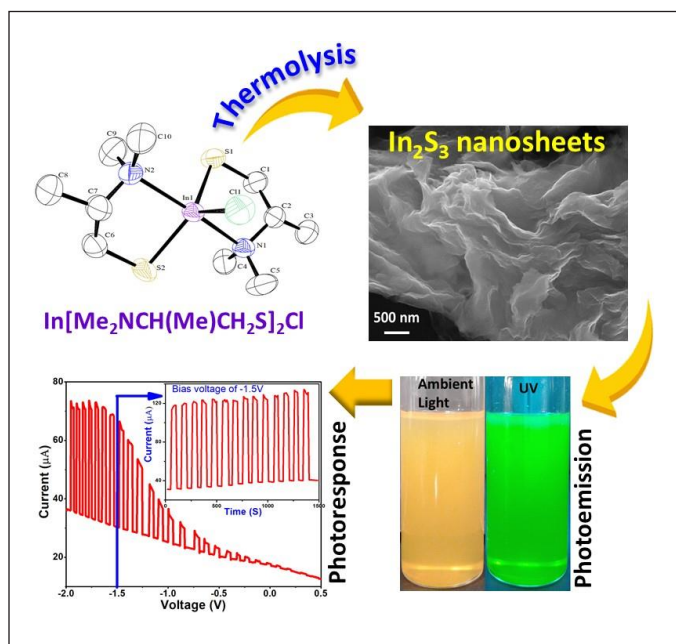
**Fig. 5.** *Synthesis of the molecular precursor In[Me₂NCH(Me)CH₂S]₂Cl for photo emissive and photo-responsive In₂S₃ ultrathin nanosheets (redrawn from reference 23).*

can be decomposed by employing various techniques also, including heat-up, hot injection, solvothermal or solventless furnace heating etc. [22]. Along with this added benefit of a SSP, there are some other inherent advantages also. For instance, existence of preformed bonds between the metal and chalcogen atoms can lead to materials with fewer defects, better stoichiometry and homogeneity. SSPs are generally air and moisture stable which gives them long shelf-life. They also have low toxicity which contribute to easy handling. Materials are obtained from a SSP at relatively low temperature, as a result of which, phase pure chalcogenide are obtained in most of the cases [23]. Finally, SSPs can also be used for the deposition of nano-structured thin films using Chemical vapour deposition techniques such as MOCVD, AACVD, LPCVD etc. SSPs are also suitable for thin film preparation by atomic layer deposition, spray pyrolysis, liquid-phase epitaxy etc. [24]. However, few challenges are also there, like, during the synthesis, it may form a non-crystalline polymer with poor solubility in common organic solvents. This makes them difficult to purify and characterize.

By adjusting the ratios of the starting reagents as well as the solvent, reaction temperature and reaction time, the size and morphology of the MC nanomaterials can be precisely controlled which finally reflects in their optical properties. Till now, many size- and shape-controlled MCs in nano-regime have been prepared through this route which include SnSe, SnS, Pd₁₇Se₁₅ and Pd₇Se₄, EuS, Ag₂Se, MnS, CoE (E = S, Se); nanoplates of SnS₂,

nanosheets of MoS₂ and WS₂, nanorods of NiS, Bi₂S₃ and Sb₂Se₃; nanoprisms of NiS; nanowires of GeS₂ and GeSe₂ have been successfully synthesized. Ternary MCs like CuInSe₂, AgIn₅S₈, Cu₁₂Sb₄Se₁₃ nanomaterials have also been synthesized by this route which are otherwise difficult to synthesize by conventional routes [25]. Karmakar et al. have synthesized an SSP: monochloroindiumbis ((2-[(dimethylamino)propyl]-1-sulfide) along with the molecular structure determination by single crystal XRD. This SSP was thermolyzed in oleylamine at 150°C for 1 minute to afford ultrathin nanosheets of In₂S₃ which exhibited photoemission and high photo responsivity which proved that they can be used as an absorber material for solar cells (Fig. 5) [26].

**Chemical vapour deposition (CVD):**

Producing high quality thin films of MCs is essential to construct flexible devices like thin film solar cells, thermoelectric devices. Moreover, material in thin film geometry provides material economy. MC materials exhibit exotic electronic properties including photo-conduction, semi-metallic behaviour and even low temperature superconduction in thin film geometry. In light of this, several techniques have been developed over the years, among which, CVD is projected to be compatible with SSPs. Complicating factors such as pre-reaction in the vapour phase can be avoided by the use of SSP for the deposition of thin films via CVD. Moreover, it's hard to match the reliability, cost-effectiveness and quality of materials offered by this method. Several techniques have been developed for thin film fabrication via CVD, depending on which, they can be categorized as metal-organic chemical vapour deposition (MOCVD), low pressure MOCVD (LPMOCVD), aerosol assisted CVD (AACVD) and atmospheric pressure CVD (APCVD). While the fundamental mechanism of CVD, i.e., formation of the desired material on a pre-heated glass/Si substrate via chemical reaction of vapour phase precursors or breakdown of SSP remains the same, it is the nature of precursors and the mechanism of its transport to the heated substrate, which varies. A "cold" wall reactor/bubbler, either made of glass or stainless steel is typically used for MOCVD, with the precursors being delivered to the heated substrate by a carrier gas [27]. However, the requirement for the precursor to be used in MOCVD is pretty stringent. Desirable properties include high purity and a reasonable vapor pressure at room temperature or below along with low cost, a low affinity for oxygen and water vapor and low toxicity. Unfortunately, finding all these qualities in a single metal organic molecule is difficult, which leaves a narrow range of precursors suitable for MOCVD. The most
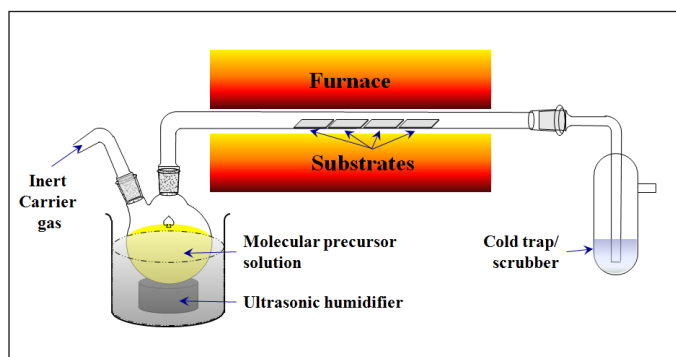
***Fig. 6.*** *Schematic diagram of a typical AACVD set-up for the synthesis of MC thin films.*

commonly used precursors were metal alkyls and/or main group hydrides, which are often pyrophoric and highly toxic. Such precursors therefore require special equipment to guard against safety and environmental hazards. As a result, SSPs suitable for MOCVD are also hard to come by. Park et al. have developed a Sn(II) complex: Sn(dmampS)$_2$ (smampS = 1-(dimethylamino)-2-methylpropane-2-thiolate) which was utilized for deposition of SnS thin films via MOCVD onto SiO$_2$ substrate at varied temperatures (300 and 350ºC) [28].

For reasons of safety, a class of MOCVD reactions are developed to operate at low pressure (LP); called LPMOCVD. The utilization of low pressure enhances the kinetic steps and allows the sublimation of solid precursors with or without a carrier gas [29]. Afzaal et al. have designed a series of asymmetric lead dithiocarbamates [Pb(S$_2$CNRR')$_2$] (R = Me, Et; R' = $^i$Pr, $^n$Bu), which acts as a suitable SSP for the deposition of PbS thin films over glass substrate. They have achieved even achieved morphology variation by manipulating the deposition temperature between 400-450°C [30].

Parallel advances in the field lead to the development of aerosol assisted CVD or AACVD (Fig. 6). In this technique, an aerosol of the precursor in a particular solvent is carried by an inert carrier gas directly into a vapourizing chamber where the solution evaporates and the precursor undergo thermal decomposition to produce thin film of the desired material over the substrate. The SSP [$^t$Bu$_2$Sn{SeC$_4$H(Me-4,6)$_2$N$_2$}$_2$] was employed by Tyagi et al. to deposit SnSe$_2$ thin film over glass substrate [31]. This method is also suitable for the deposition of multinery MCs as several precursors can be dissolved in the same solution and the aerosol containing all the SSPs can be delivered at once to the substrate, which can be considered as an added advantage. This class of assisted CVD techniques also include liquid injection CVD and spray pyrolysis techniques, which also employs SSPs for high quality thin film deposition.

## Summery and Future Prospect

The vast application of MCs in the future of energy harvesting and energy storage materials require the discovery and development of synthetic strategies which are fast, easy to scale up with the added benefit of economic in nature. In particular, reproducibility of results in newly developed synthetic route is very important aspect as slight variation in the composition or morphology in MCs can affect their electronic properties to a great extent. This article focuses on various classical and modern synthesis routes for the fabrication of MC nanomaterials and thin films. Comparison of various protocols has also been discussed which is quite important. Along with general discussion and comparison, several examples of each and every synthetic method have been incorporated to provide a better understanding and synthesis-property correlation. However, inheriting to the existing synthetic methods only will not do justice to the scientific field. Thus, development of new and advanced synthetic strategies in future to generate high-quality MC nanomaterials and thin films are equally important. Vigorous efforts to understand the relation between the underlying nucleation and growth mechanism and the final properties of the MC materials should be made to design desired MC nanomaterials rather than just the preparation of them.

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**Dr. Gourab Karmakar** *received his Ph.D. degree in Chemistry from HBNI, Mumbai, after joining chemistry Division, BARC as a Scientific Officer (C) in the year 2016. Since then, he is actively involved in the design and development of efficient single source molecular precursor for metal chalcogenide nanomaterials and thin films. He has published several research papers and conference papers as well and presented his research work at various scientific platforms.*

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