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Review Article

Solid State and Materials Research in India

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The current status of research in the area of solid state and materials chemistry in India have been presented and discussed. The article focuses on various materials that have been categorized as traditional solids (*dense*) and *porous* solids. While many of the material properties such as ferromagnetism, superconductivity, colossal magneto resistance, multiferroic behaviour, etc. have been explored mainly in dense solids, porous solids contribute towards many properties in the areas of catalysis, sorption, gas separation and hydrogen storage. Possible directions for future research, along with identifying and highlighting the strengths of the expertise available in this country, were also mentioned.

Keywords: Structural Characterization; Materials Chemistry; Superconductivity; Nanomaterials

Introduction

Solid state chemistry as a subject has been in existence for many years. The systematic study of synthesis, structural characterization of solids and their structure-property correlations during the 60s can be considered to be the beginning of solid state chemistry. Conventionally, synthesis, structure and characterization (mainly investigating electronic and related properties) constituted the main focus of research in solid state chemistry. Over the years, considerable effort was undertaken to classify the solids based on the observed properties (Rao, 2013; West, 1985). When a solid is endowed with useful properties, then it becomes a *material* that could have practical applications. The traditional classification of the solids is based on the electrical response to the flow of current, which results in conducting, semi-conducting, insulating and superconducting solids. Over the years, the availability of advanced characterization facilities found many solids with improved properties, which paved way for the development of a new area of research – now known as Materials Chemistry, which includes organic and hybrid materials. Today, the number of journals that deals with materials chemistry are considerably larger than those dealing with traditional solid state chemistry. Materials chemistry is now firmly established as an interdisciplinary area of research where scientists across disciplines (basic sciences and engineering) collaborate to develop new materials with interesting and useful properties.

Additionally, the evolution of solids with large open spaces, cavities and channels (porous solids), which find significant applications in the areas of sorption, separation and catalysis, also provided an impetus for a change in the classification of solids. In recent years, many of the classical solids have also been prepared as nanomaterials. The development of nanomaterials and their applications draws from the knowledge gained over the years during the development of solid state and materials chemistry. This indicates the impact the solid state chemistry has on new materials. The strength of solid state chemistry is that many of the compounds are environmentally benign and stable, which can be harnessed for advanced device applications. Presently, thesolid materials can broadly be classified as *dense*, *porous* and nanomaterials. Tailoring specific property in solids (electrical, magnetic, dielectric, etc.) is important from the point of view of utilising them in

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solid state devices.

In the present compilation, we present and highlight the recent developments that have taken place in the area of solid state and materials chemistry in India. The topics have been chosen to provide an overview of the current trends and developments in this area (during the last decade or so) – it would be difficult to cover each and every aspect of research in the area of solid state and materials chemistry. We have also highlighted the importance of dense materials in magnetic, electrical, dielectric, multiferroic, superconducting, optical and other related properties. The porous solids, on the other hand, provides the basis for catalysis, sorption and gas separation. The porous solids are generally used in the oil industry, especially in cracking of crude oil and in producing fine chemicals. In addition, the newly developed porous solids, the metal-organic frameworks, exhibit good gas separation, sorption as well as hydrogen storage. Much of the developments in the area of materials appear to orient towards energy due to the concerns on the status of fossil energy. There is an urgent requirement for developing newer materials that would address the future energy requirements. The research and advancements on nanomaterials would be outside the scope of this article.

Dense Solids

In this section, we present the developments that have taken place in the chemistry of dense materials. Solids containing transition metals constitute one of the most interesting class of materials, which exhibit a wide variety of structures and properties. The excitement surrounding the observation of magnetism in the mineral magnetite, Fe_3O_4, by the ancients continues even today. The various developments that have taken place over the years in the synthesis approach makes it possible to design and prepare new materials with defined magnetic behaviour. The impetus for research in this area, of course, is driven by the use of magnetic solids as hard drives in computers and related purposes. The use ofthe charge and the spin in a magnetic solid and its quick response to the applied field are important for information storage. This area of research is now known as *spintronics*. The current trend of research has been on exploring materials that can produce energy and store energy. The areas of interest include recently discovered organic-inorganic hybrid materials, battery, thermoelectric, photocatalytic, magnetic, superconductive, ferroelectric and multiferroic materials.

Among the various renewable energy sources, solar energy is most abundant and a clean source of energy. Generally, silicon and other compound semiconductors have been used in photovoltaic cell for the conversion for light energy into electricity. Recently, a hybrid perovskite material $CH_3NH_3PbI_3$ that combine organic and inorganic blocks was shown to exhibit solar cell efficiency of more than 22% with much higher absorption strength than the inorganic semiconductors (Kojima *et al*., 2009). Following this report, several groups in India have been actively involved in exploring new hybrid materials for solar cell applications. The research group of Sarma (Govinda et al., 2018), Narayan (Singh *et al*., 2017) and others (Biswas *et al*., 2017; Sahastrabudhe and Bhattacharya, 2015; Sarkar and Mahadevan, 2017) have investigated the hybrid perovskite system of compounds during the past few years, which resulted both in the discovery of a rich diversity of compounds as well as a better fundamental understanding of many properties. In addition to the experimental studies, there have been reasonable theoretical studies augmenting the experimental observations (Nagane *et al*., 2014). Fabrication of solar cells based on the halide perovskites have also been initiated (Halder *et al*., 2015).

An alternative to photovoltaics is the photochemical splitting of water to generate hydrogen, which is a clean source of energy. Solar photochemical splitting of water uses semiconductor light absorbers and co-catalysts. The other approach is a solar-thermochemical process that provides a high theoretical efficiency and the use of the entire solar spectrum allows large scale production of H_2 (Rao and Dey, 2016) Rao and co-workers investigated both photochemical and thermochemical methods of hydrogen production employing a number of semiconductors and mixed valent transition metal oxides (Rao and Dey 2017). Chemically modified wide band gap semiconductors such as $ZnO/Pt/Cd_{1-x}Zn_xS$ have been shown to exhibit good hydrogen evolution using visible light (Lingampalli, Gautam and Rao, 2013).

Another area related to energy is the studies

involving Li/Na ion migration towards the development of new battery materials. The development of lithium ion batteries has been pioneered by the research efforts on intercalation chemistry in two-dimensional structures such as $LiCoO_2$, TiS_2 and graphite (Whittingham, 2004; Blomgren, 2017; Whittingham, 2004). Many research groups have contributed to the development of Li-ion electrode materials (Vellaisamy and Nallathamby, 2015; Prakash *et al*., 2010; Bhaskar *et al*., 2012). The researchers from CECRI have demonstrated high capacity (~300 mAh/g) in lithium rich layered oxides (Sathiya *et al*., 2013). Barpanda and coworkers have been investigating polyanionic compounds such as alluaudite-$Na_2MnFe_2(PO_4)_3$, $NaCo(PO_3)_3$ and $NaFe(PO_4)_3$ as potential cathode materials for Na-ion battery materials (NIB) (Gond *et al*., 2017; Dwibedi *et al*., 2018; Gond *et al*., 2018). Martha and coworkers have developed a new electrode architecture made of silicon and carbon as anodes for Li-batteries with reversible capacities of ~2,000 $mAhg^{-1}$ (Krishna Kumar, Ghosh, Martha, 2017). The combination of the cathode and the newly developed anode materials in a coin-type lithium ion cell was found to exhibit energy densities of 500 Whg^{-1}, which is high compared to the commercially available ones.

Thermoelectric materials can directly and reversibly convert waste heat into electricity, and are expected to play a significant role in the future of energy management. To discover a new thermoelectric material would demand a combination of keen chemical intuition, synthetic expertise, materials processing as well as good measurement skills. Biswas and co-workers have prepared a new class of inorganic metal chalcogenides such as AgCuTe, SnTe and GeTe, which exhibit good thermoelectric behaviour. These compounds have been shown to convert waste heat to electricity with efficiency in the range of 12-15 % (Samanta and Biswas, 2017; Roychowdhury *et al*., 2015; Perumal *et al*., 2015; Roychowdhury *et al*., 2018).

Tyagi and co-workers have developed many new compounds stabilized in the well known crystal structures of rutile, fluorite, perovskite and pyrochlore types. Many of the compounds have been shown to exhibit interesting properties towards the treatment of nuclear waste (Shukla *et al*., 2009; Shukla, Arya and Tyagi, 2010; Shukla *et al*., 2013; Achary *et al*., 2009). The discovery of high temperature superconductivity in cuprates created much enthusiasm to investigate many related compounds. One such compound is LnOFeAs, which is based on the layered BiS_2 containing pnictide and chalcogenide. Ganguli and co-workers have extensively investigated the superconducting properties in Fe containing oxypnictide super-conductors using cation and anion substitution in LnOFeAs based superconductors. New members of Eu-based BiS_2 compounds, $EuSr_2Bi_2S_4F_4$ and $Eu_2SrBi_2S_4F_4$ were shown to exhibit T_c up to 3.5 K with Se–substitution (Prakash and Ganguli, 2011; Arumugam *et al*., 2017; Haque *et al*., 2018).

An area that attracts interest is the study of the interplay of ferromagnetism and ferroelectric behaviour in the same solid – known as *multiferroics*. The observation of ferroelectricity, which requires a second order Jahn-Teller effect (off-center displacement of d^0 cations) and ferromagnetism, which requires partially filled d shells, have mutual incompatibility. It is clear that to have compounds exhibiting multiferroic behaviour a different rational approach would be required. The participation and use of stereoactive lone-pairs could be of potential use in the observation of ferroelectricity. Besides multiferroic properties in a single phase material also need to satisfy stringent symmetry requirements. Sundaresan and co-workers demonstrated linear magnetoelectric behaviour in spinel oxides, MnB_2O_4 (B=Al and Ga), Co_3O_4 and R_2BaCuO_5 (R=Sm and Dy) containing magnetic ions at the noncentro symmetric site (Saha *et al*., 2016; Ghara, Ter-Oganessian and Sundaresan, 2017). A new approach involving coupled magnetism and ferroelectricity has been demonstrated in $RFeWO_6$ (R= Eu, Tb, Dy and Y) where a noncollinear but commensurate spin structure is sufficient to show magnetoelectric coupling (Ghara *et al*., 2017). New synthetic protocols for the preparation of materials and examining the properties are being pursued by Sebastian, Nagarajan, Uma and co-workers (Mishra *et al*., 2018; Tripathi and Nagarajan, 2017; Nagarajan *et al*., 2016)

The studies on optical property on solids have been limited. In recent years, Natarajan and co-workers have been actively engaged in studying the optical properties on transition metal substituted oxides towards developing new colored inorganic solids (Bhim *et al*., 2017; Tamilarasan *et al*., 2016; Laha *et*

al., 2016). Many of these compounds have transition elements in unusual/distorted coordination environments, which give rise to allowed $d - d$ transitions resulting in unusual and new colors, which are of interest as inorganic pigments. These compounds are environmentally benign.

Advancements in computational facilities has created opportunities to explain many observed properties theoretically. Waghmere, Pati and co-workers have used *first-principles* (non-empirical) calculations, modelling and computer simulations effectively in obtaining fundamental insights into microscopic mechanisms that govern multi-scale behaviour of a wide range of materials and prediction of new materials with technologically important properties (Shirodkar and Waghmare, 2014; Anand, Thekkepat and Waghmare 2016; Waghmare, 2014; Gros *et al*., 2004). Many other groups have also actively contributed to the development of the theoretical approaches in the understanding of the many observed properties in the solids (Samanta, Kar and Saha-Dasgupta, 2016; Tarafder *et al*., 2012).

Porous Solids and Catalysis

Porous solids have emerged to occupy an important area of research in chemistry of materials. The fascination of a 'boiling stone' (zeolites) in the 17th century continues even today. These are special solids whose properties arise from their porous architecture. Porous solids can be broadly classified based on their pore sizes. Thus, zeolites (aluminosilicates), aluminophosphates and other related compounds with pore diameters in the range 2-20 Å are known as microporous materials, compounds with pore sizes in the range 20-100 Å are known as mesoporous materials and compounds with pore sizes >100 Å are classified as macroporous materials.The family of porous solids now have compounds that include most of all the metals of the periodic table. Of these, the aluminosilicates are the most important and widely studied family of compounds, as they possess good thermal stability.

During the last two decades another class of compounds that combine the ideas of inorganic and organic chemistries have been developed. These are compounds that combine the coordination variability of inorganic metal ions and functional diversities of organic ligands to give rise to robust open structures with large pores. They are known as metal-organic framework (MOF) compounds. These are crystalline solids with three-dimensionally extended structures in which the metal ions or clusters are connected through molecular bridges. The compounds combine the coordination versatility of the central metal ions and the functionality of the bridging organic molecules. The structures retain the integrity of the building blocks, the chemical functionality as well as the rigidity during the synthesis. The pore size control has been achieved by incorporating non-volatile guest species or by creating interpenetration or interweaving within the structures. The metal organic frameworks have weaker bonds, which opens up the possibility of creating solvent driven structural transformations. In addition to utilising the coordinatively unsaturated metal centers, the MOF compounds also offer the possibility of functionalising the bridging ligands. In a sense, the MOFs offer the advantages of both the organometallic and the organic chemistry, which is unique. Some of the MOF structures have been shown to be good adsorbents for hydrogen, which opened up this area further and created much interest towards hydrogen storage materials. The possibility of producing chiral frameworks and chiral structures are challenging and interesting.

Considerable progress has been achieved in the studies of MOFs in India. Many practicing coordination chemists of India saw the opportunity in MOF based compounds and switched their focus to this exciting new class of materials that appear to offer much scope for practical applications in the areas where aluminosilicate zeolites have been traditionally employed. The Indian contributions are both important and significant due to the presence of a number of researchers in the area of coordination chemistry. Here we present the highlights of few researchers who have made good contributions.

Maji and coworkers mainly focuses on materials that may have direct impact in the chemical industry such as cost-effective separation of different chemical feedstock (separation of geometrical isomers such as xylenes, styrene/ethylbenzene or benzene/cyclohexane) and removal of toxic heavy metal ions from aqueous solution. By employing a new approach and measurement setup, Maji and his group have demonstrated the separation of CO_2 from CO_2/N_2 or CO_2/CH_4 mixtures and C_2H_2/C_2H_4 (1:99, V/V) which

have significance for chemical industry. He has recently been focusing on downsizing the MOFs into nanoparticles, which is expected to have better stability and also usability in industries (Sutar *et al*., 2018; Hazra *et al*., 2017; Roy *et al*., 2018). Bharadwaj and co-workers concentrate on the supramolecular assembly of cryptands for use as smart materials as well as preparing new metal-organic frameworks (MOFs) for gas sorption and Lewis acid catalysis. His work on the single-crystal to single-crystals transformation of MOF structures during ligand/cation exchange and removal of solvent molecules are important (Sharma, De and Bharadwaj, 2018; Sharma *et al*., 2017; Verma, Tomar and Bharadwaj, 2017).

The excitement created by the discovery of new porous compounds and exploring the many properties such as gas sorption, separation, catalysis in the MOFs compounds, generated interest in the study of another class of compounds that are based purely on organic chemistry. These compounds are classified as covalent organic framework (COFs) compounds. These are two-dimensional polymeric compounds and offer good thermal stability along with acid and base resistance. The study of polymers and polymer chemistry has been well established over the years in India, but active research in the area of COFs was taken up only during the last 10 years. Banerjee and co-workers concentrates on hydrogen storage and carbon capture and developed methodologies for synthesizing covalent organic frameworks with good chemical stability. The porous COFs have also been explored for gas and liquid separation application. His group also prepared COFs as nanomaterials (hollow spheres and nanorods). The COFs are based on polymeric assemblies, which may find use as good proton conducting porous crystalline membranes that may replace the Nafion membrane in fuel cells (Dey *et al*., 2017; Karak *et al*., 2018; Kandambeth *et al*., 2017).

Selvam and co-workers employ a number of synthetic routes for the preparation of a ordered porous (micro-, meso- and hierarchical) materials (zeolites and zeo-types). Typically, the porous structures comprise the silicates, aluminosilicates, aluminophosphates, aluminates, carbons, and a variety of binary and ternary metal oxides, etc. The morphologically-controlled noble metal clusters have also been anchored within the pores for supported catalysts (Kumar, Krishna and Selvam, 2019). The NCL, Pune is an important centre for catalytic research in India, where both heterogeneous as well as homogeneous catalysis is being carried out. Presently, Gopinath, Srinivas and their co-workers are continuing the tradition of employing aluminosilicates, mesoporous silicas, supported metal catalysts for their studies (Patra, Bhuskute and Gopinath, 2017).

Points to Ponder

The above compilation makes it amply clear that the solid state and materials chemistry offers immense possibilities for advanced studies and research. This is an ever expanding and exciting area of research and holds much promise for future. At this juncture, it is pertinent to point out certain lacunae that needs to be considered for further development. First and foremost is the need to develop new methodologies for synthesis, especially targeted synthesis towards solids with specific functionalities. In addition, to continue the developments witnessed in solid state and materials chemistry, a sustained support and encouragement for exploratory synthesis is also required. The compounds (solids) prepared in a laboratory need many characterizations to evaluate the properties and it requires active collaborations with researchers of other disciplines such as physics, engineering etc to name a few. This again needs to be encouraged and supported actively to enhance the outcome of studies/research. Another area that require consideration is the teaching of the subject itself – though solid state and materials chemistry has been an active area of research for more than five decades, it has not been taught as a subject in many higher educational Institutions – there needs to be active promotion of this subject. The last point is with regard to the basic research facilities in this area. The main constraints in characterizing a newly prepared solid is to identify the structure, which would require advanced X-ray facility such as a high power synchrotron and neutron. In addition, the lack of accessibility to characterization tools such as high-resolution transmission electron microscopy (HRTEM), X-ray absorption (EXAFS) and photon electron spectroscopy (XPS) and other related equipments impedes research in this area. Many of these require considerable financial considerations and support and it would help in setting up central

characterization facilities in different parts of the country – allowing easy access to many researchers.

The above are the bottlenecks in the development of solid state and materials chemistry as an important area of study – few suggestions are listed here that might alleviate this aspect. It may be worthwhile to support national workshops (preferably every year) that involve hands on training for young researchers from different parts of the country. The workshop could cover the basic aspects of solid state and materials chemistry such as synthesis, structure, electronic/magnetic/optical properties. It would help the researchers if hands-on training is also imparted. A online resource providing guidance on the availability of expensive instruments/facilities would help in accessing them. A central facility, supported by generous funding from the Government, where samples can be sent and the results are obtained over the internet can be created to speed up the research outcome.

Concluding Remarks

A brief overview of the current scenario of materials chemistry is presented here, albeit constrained by the limitations of the authors, brings out the immense research opportunity that exists both in experiment as well as theory, which in our opinion should go hand in hand to make tangible progress. As part of this article, we have also pointed out some of the fruitful directions of research in this field that could be pursued profitably by young researchers continuing research in this area. While the practice of theory in this field has largely been *aposteriori*, what is required is theory with reasonable predictability. Of course, we do realize that it is a tall order for the field of chemistry, more so in the field of solid state and materials.

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