Current trends in chemistry of materials

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The many facets of research in the area of solid state materials chemistry have been presented and discussed. The article focuses on the present status and broadly concerns dense and porous solids. While many of the materials properties such as ferromagnetism, superconductivity, multiferroic behaviour and so on have been explored mainly in dense solids, porous solids contribute towards many properties in the areas of catalysis, sorption, gas separation including hydrogen storage. The article describes the current status of activity with regard to energy materials as well as creating materials (synthesis and the role of chemistry) and understanding materials (the role of theory). Possible directions for future research along with identifying and highlighting the strengths of the expertise available in this country are also mentioned.

1. Introduction

Solid state materials chemistry as a distinct discipline of chemical sciences has been in existence for many years [1]. The systematic study of correlating the properties with the structures of solid compounds during the 60s has been regarded as the beginning of solid state chemistry. This area now encompasses a healthy interface between chemistry, physics and biology. Conventionally, a study of synthesis, structure and properties of solid compounds constitutes solid state chemistry and there has been considerable effort in classifying the solids based on the observed properties [1,2]. A solid endowed with useful properties 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 and has been in terms of conducting, semi-conducting, insulating and superconducting solids. The discovery of transistor behaviour [3], which revolutionized the thinking process with regard to the solids, could be taken as an important step in this direction. The more recent discovery of superconductivity in compounds based on copper oxides is a landmark event in solid state chemistry research [4]. This is a remarkable collective electron phenomenon in solids, arising from the formation of pair of electrons that permit the flow of electric current without resistance. Over the years, the observation of many properties in the same solid necessitated a change in the classification. In addition, the evolution of another class 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. Presently, solid materials can broadly be classified as dense and porous solids.

Tailoring specific property in solids (electrical, magnetic, dielectric, etc.) is important from the point of view of utilising the solid as a material. Recent developments have provided a variety of new materials that include thermoelectric materials [5], superconducting materials [4], ferroelectric materials (multi-ferroic materials) [6], materials for hydrogen storage (energy materials) [7] inorganic-organic hybrid materials [8] and materials for other related properties. In this context, one needs to appreciate the importance of one structural family of dense solids, viz., perovskites, ABO₃, (figure 1) for being the

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Figure 1. The perovskite structure along with some of its layered variants. (a) the perovskite, SrTiO$_3$ (b) the Aurivillius phase, Bi$_4$Ti$_3$O$_{12}$ ([Bi$_2$O$_2$]$A_{n-1}B_n$O$_{3n+1}$] (c) the Ruddlesden–Popper phase, Sr$_4$Ti$_3$O$_{10}$ ($A'_2[A_{n-1}B_nO_{3n+1}]$) and (d) the Dion–Jaconson phase, CsCa$_2$Nb$_3$O$_{10}$ ($A'[A_{n-1}B_nO_{3n+1}]$).

platform for realizing many of the materials properties. Perovskite structure can be described as formed by the corner sharing of the BO$_6$ octahedra with the A ions being accommodated at the cubo-octahedral site [1,2]. The structure can exhibit considerable flexibility in terms of dimensionality and accommodate many elements as part of the structure, which is one of the reasons for the observation of many important properties in this family of compounds. In table 1, we list some of the important properties exhibited by the compounds that are formed with the perovskite related structures.

In this article, we propose to outline the various developments that have taken place in the area of chemistry of materials in recent years. The various sub-topics have been chosen such that the reader is aware of the current trends and developments in the area of chemistry of materials. In doing so, we have highlighted the importance of dense materials in magnetic, electrical, multiferroic, superconducting and other related properties. Such materials find use in communication, data storage, etc. The porous solids, on the other hand, have been the work-horse for catalysis and in the oil industry, especially the cracking of crude, etc. It has been shown that the porous solids are excellent materials for gas separation, sorption and hydrogen storage. Many of the developments in materials appear to be oriented towards energy as fossil energy is fast depleting and there is an urgent need for developing newer materials. The properties exhibited by a solid crucially depend on the synthesis and the role of chemistry in fine tuning the properties is also highlighted. In addition, attempts have been made to indicate the major milestones in the development of the theoretical understanding of such materials as well.

2. Dense solids: Magnetic, electrical, multiferroic and superconducting materials

In this section, we give the recent developments that have taken place in some of the important areas of chemistry of dense materials. Conventional magnetic materials are mostly dense inorganic solids. The excitement surrounding the observation of magnetic behaviour in the mineral magnetite, Fe$_3$O$_4$, by the ancients continues even today. Structure-property correlations in magnetic materials were investigated by many researchers and particularly by van Vleck, Mott, Hubbard, Stoner, Anderson, Goodenough and Kanamori and many others [9]. Based on the principles of crystal chemistry, it is now possible to design and prepare many molecular materials with defined magnetic behaviour. The impetus for research in this area is driven by the use of such solids as hard drives in computers and related purposes. The combination of charge and spin information in a solid and its response to the applied field were important for information storage and related purposes. This field is known as spintronics and generally semi-conducting and half-metallic ferromagnetic solids exhibit this type of behaviour [10]. Based on the understanding of magnetism in solids, we are now in a position to contribute to this area significantly.

Recently, there is much interest in the study of the interplay of ferromagnetism and ferroelectric behaviour in the same solid. The observation
of ferroelectricity, which requires a second order Jahn–Teller effect (off-center displacement of d\(^2\) cations) and ferromagnetism, which requires partially filled d shells, appears to have mutual incompatibility. If the two properties need to be combined, one needs to investigate systems containing partially filled d-shells of the transition metal ion (ferromagnetism) along with a different mechanism for the observation of ferroelectric behaviour. In the light of this, the participation and use of stereoactive lone-pairs in observing ferroelectric behaviour is important. Thus, the combination of Mn\(^{3+}\)/Fe\(^{3+}\) ions and stereoactive lone-pair of Bi\(^{3+}\) has given rise to BiMO\(_3\) (M = Mn, Fe) oxide compounds, which exhibit multiferroic behaviour [11]. One needs to note that the multiferroic materials discovered till now do not have both the large polarizations and the magnetizations simultaneously above room temperature. The use of f-electron magnetism (rare-earths) along with second-order Jahn–Teller effect could provide useful avenues for future research.

Materials that exhibit conducting properties remain a focus of intense scientific research for both fundamental as well as for application related purposes. Research on the study of conducting materials, especially superconducting ones, has undergone a major change after the breakthrough of cuprate superconductors with superconducting transition temperature above 40 K, 20 years ago (figure 2a) [3]. In this light, it may be pointed out that the original theory proposed in 1957 for understanding the superconducting behaviour in a solid, the BCS theory [12], does not predict superconducting transition temperatures above 30 K. Thus, the discovery of cuprate superconductors is important not only in overcoming the crucial barrier in terms of the transition temperature, but also it provided a good opportunity to experiment solid state chemistry with other related phases. This resulted in many different variants of structures based on layered copper oxides. Search for new superconducting materials constitute an area of research where solid state chemists can play a major role. This results in new discoveries as well as materials where one could test the theoretical predictions. In table 2, we list some of the important superconducting materials that have been discovered during the last 10 years. The observation of superconducting behaviour in materials that have two-dimensional character (layered solids) suggests that electron-phonon coupling could be one of the reasons and it is believed that superconducting properties in solids can be observed even at 450°C (figure 2b). This could be a tremendous boost to experimental researchers to expand the scope for search of newer materials via novel synthetic approaches.

Materials that have high dielectric constant (\(\varepsilon\)) are in constant demand because of their application as capacitors in microcircuits among others. In addition, due to the desirability to have smaller electronic devices, the highly insulating solids are employed as interlevel dielectrics (ILD)

### Table 1. List of the important properties exhibited by the perovskites based solid materials.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Property/Phenomenon</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Metal (metallic conductor)</td>
<td>LaNiO(_3)</td>
</tr>
<tr>
<td>2</td>
<td>Superconductivity</td>
<td>(Ba,K)BiO(<em>3), La(</em>{2−x})Sr(_x)CuO(_4)</td>
</tr>
<tr>
<td>3</td>
<td>Ferroelectricity</td>
<td>BaTiO(_3), PbTiO(_3)</td>
</tr>
<tr>
<td>4</td>
<td>Relaxor ferroelectricity</td>
<td>Pb(_3)MnNb(_2)O(_9)</td>
</tr>
<tr>
<td>5</td>
<td>High temperature ferroelectricity</td>
<td>Bi(_4)Ti(_3)O(_12)</td>
</tr>
<tr>
<td>6</td>
<td>Piezoelectric</td>
<td>PbTi(_{1−x})Zr(_x)O(_3)</td>
</tr>
<tr>
<td>7</td>
<td>Ferromagnetism</td>
<td>SrRuO(_3)</td>
</tr>
<tr>
<td>8</td>
<td>Jahn–Teller effect/orbital ordering</td>
<td>LaMnO(_3)</td>
</tr>
<tr>
<td>9</td>
<td>Colossal magnetoresistance</td>
<td>La(_{1−x})Sr(_x)MnO(_3)</td>
</tr>
<tr>
<td>10</td>
<td>Luminescence</td>
<td>K(_2)La(_2)Ti(_3)O(_10); RE</td>
</tr>
<tr>
<td>11</td>
<td>Spintronics/half-metallicity/ferromagnetism</td>
<td>Sr(_2)FeMoO(_6)</td>
</tr>
<tr>
<td>12</td>
<td>Fuel-cell electrode</td>
<td>Sr(_2)(Mg,Mn)MoO(_6)</td>
</tr>
</tbody>
</table>

### Table 2. List of new superconductors discovered since 2000 along with the \(T_c\).

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Material</th>
<th>Year of discovery</th>
<th>(T_c) (max., K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sr(_2)RuO(_4)</td>
<td>1994</td>
<td>(\sim 1)K*</td>
</tr>
<tr>
<td>2</td>
<td>MgB(_2)</td>
<td>2001</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>Na(_2)CoO(_2), yH(_2)O</td>
<td>2003</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>Y(_2)C(_3)</td>
<td>2004</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>CaC(_6)</td>
<td>2005</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>LaO(_{1−x})Fe(_x)FeAs</td>
<td>2007</td>
<td>36</td>
</tr>
</tbody>
</table>

*p-wave (spin-triplet) superconductor [58].*
to separate the conducting parts from one another. These solids also find applications as gate dielectrics in integrated circuits (IC) and also in memory elements in microcomputers such as DRAM and FeRAMs. The recent discovery of CaCu$_3$Ti$_4$O$_{12}$ with high $\kappa$ (>10,000) appears to hold much promise [13].

3. Porous solids

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 [14]. The family of porous solids now have compounds that include most of...
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.

The aluminosilicates are solids possessing regular pore architecture and exhibit a variety of properties such as ion-exchange, separation and catalysis. Many of these properties arise from the size of the pore window, the accessible void space and the dimensionality of the channel system. The empirical formula for an aluminosilicate zeolite can be expressed as \( A_{x/n}[Si_{1-x}Al_xO_2] \cdot mH_2O \), where \( A \) is a metal cation of valence \( n \), which is generally located along with the water molecules in the channels and can be easily ion-exchanged (figure 3a) [15]. One of the important characteristics of these compounds is that they avoid \( Al – O – Al \) linkages (known as the Lowenstein’s rule). The zeolites have been the main catalysts for many industrial catalytic processes [16]. The functionalization of the channels within the zeolites, preparation of supported oriented thin films, synthesis of polycrystalline membranes, colloidal zeolites with narrow particle size distribution are important developments in this area [16]. Of these, the nanozeolites are important as they offer high external surface areas and activities, shorter diffusion pathways and accessible catalytic sites. Since the particle surface can be functionalized by organic groups, these can be dispersed easily in organic medium and also can be used for building extended structures. The main problems with the use of zeolites with small sizes (nano-sizes) are their low synthesis yields and inconsistent reproducibility. Chiral zeolites are another important class of materials that are used for chiral catalysis, but the difficulties in resolving enantiopure zeolites still persist.

The discovery of aluminophosphates (AlPO), AlPO₄, in 1980s with reasonable thermal stability and novel structures is an important development in this area [17]. AlPOs offer the possibility of substituting \( Al^{3+} \) by bivalent ions such as Mg, Zn, Co, etc. (MeAlPO) and at the \( P^{5+} \) sites by tetravalent Si (SAPO), which can incorporate acidic protons. In addition, the possibility of generating redox centers in MeAlPOs along with the availability of acidic protons can be utilized for the oxidation-reduction and the acid catalysis simultaneously [18]. The oxidation of terminal carbons in a linear alkane at moderate temperatures and pressures to form the corresponding acids has been demonstrated [18]. This and many other related studies have demonstrated the efficacy of the use of AlPOs in industrially important processes (figure 3b). The lower thermal stability along with reduced recyclability, however, impedes the progress in the use of AlPOs commercially.

![Figure 3](image-url)

This discovery, however, opened up many important vistas for investigating other related phases that lead to an explosive growth of framework phosphate structures [19].

In the 1990s, porous metal-organic frameworks (MOF) provided another important development in this area [20–23]. These are crystalline solids with three-dimensionally extended structures in which the metal ions or clusters are connected through molecular bridges (figure 4a). These are compounds that combine the coordination versatility of the central metal ions and the functionality...
and its properties have been well established, the use of such arrays for preparing new types of compounds is a paradigm shift in synthetic inorganic chemistry. The use of surfactants, block copolymers and liquid crystals as templates for the formation of new forms of silicas with diverse mesoporous structures has opened up this area as such forms are not possible with zeolite synthesis (figure 5) [24,25]. The important aspect of these structures is that the surface walls of many of the mesoporous compounds are amorphous as they are formed by hydrolysing silica esters over the micellar assembly. Many of the mesoporous compounds are investigated and characterized using high resolution electron microscopy. Using micellar arrays, powders, nanoparticles, self-standing thin films and supported films, monodispersed spheres and monoliths have been prepared. Surface functionalisation in mesoporous silicas either during the synthesis or by post-synthesis procedures is possible. Since the micellar chemistry is

of the bridging organic molecules. The interesting aspect of these structures is that they retain the integrity of the building blocks, the chemical functionality and rigidity during the synthesis. Control of the pore sizes has been achieved by incorporating non-volatile guest species or by creating interpenetration or interweaving in 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 (figure 4b). The possibility of producing chiral frameworks and chiral structures are challenging and interesting.

The use of surfactants for controlling the formation of structures was established in the early 1990s. Though the chemistry and physics of micelle

Figure 4. Structures of the mesoporous silica material. (a) MCM-42 and (b) MCM-48. The extra-large pore sizes can be utilised for many important applications (see text).

Figure 5. (a) The structure of metal-organic framework structure, [Zn₄O(1,4-bdc)(DMF)₈(C₆H₅Cl)]. (b) The hydrogen absorption on the above compound.
well understood, the mesoporous compounds have transitioned from synthesis towards applications and commercialization. Some of the mesoporous compounds find applications in low-k dielectrics, catalysis, separation, optics, magnetics, sensing, etc. The development of periodic mesoporous organic silicas (PMOs) along with the preparation of non-silicate mesoporous compounds has generated considerable interest in this area. The carbon replicas of the mesoporous silica are another exciting development as they can be used as electrode materials in secondary lithium batteries, supercapacitors and biosensors [26]. The mesoporous carbon lacks the ease of surface functionalization, which needs attention. In addition, an understanding of mesostructural organization, defects, grain size and nucleation processes are important for advanced engineering and utilisation of these solids.

The macroporous materials with pore sizes greater than 100 Å are important for their enhanced mass transport of the guest species and reasonable space for pore wall modifications. The pore wall modifications include the internal surface modifications using functional groups, small molecule anchoring and nanoparticle coatings. It has been shown that such functionalisation can be utilised for useful catalytic studies. These compounds also offer possibilities for obtaining hierarchical structures and multifunctionality. The three-dimensionally ordered macroporous solids with wide ranging properties that include insulating, semiconducting, conducting (metallic), etc. have been synthesized using the colloidal crystal templating technique [27]. The macroporous solids with length periodicity in the range of visible radiation can function as photonic crystals. The other applications of the macroporous solids are in the areas of bioglasses, catalysts and battery materials. One of the challenges in forming macroporous compounds is to obtain structures that are not cubic. In addition, it is also preferable to be able to control the defects so as to use them for optical studies.

4. Materials for energy conversion and storage

The problems associated with the anticipated depletion of the fossil fuels in the near future have generated considerable interest in the study of energy materials. The need for alternative energy sources and efficient ways of generating power is important. The vast knowledge gained on the study of the structure-property correlations in the area of catalysts, batteries, fuel cells, thermoelectric and optical materials would be fruitfully utilized in designing newer and efficient materials for energy.

4.1 Catalysts

In the area of catalysts, the main challenge is to prepare new materials that would be utilized for the selective oxidation of alkanes and also for the conversion of methane to higher hydrocarbons [28]. The development of new electrocatalysts for fuel cells is also a priority. One of the important clues for developing new materials for emerging needs is to fine-tune the ion mobility and electronic defects in a solid. The oxygen and hydrocarbon adsorption, activation and redox processes depend on the structure and composition of the surface of the solid/oxide and our present understanding of the surface structures has not reached a state where we can predict the performance of the catalysts. This is a very important issue for future research.

4.2 Battery materials

The discovery of redox lithium ion mobility in layered LiCoO$_2$ is an important landmark in the area of battery materials. The development and commercialization of LiCoO$_2$/graphite cell directly resulted from the contribution of the solid state chemists, which enabled the portable electronic devices as an integral part of the society. The LiCoO$_2$ based cell is generally used for low power applications. The requirements for high power applications such as batteries for electric vehicles, where nickel-metal hydride batteries are used, remains a challenge. The discovery of nanomaterials and nanocomposites are important developments in this area as the nanocomposites can absorb stress and strain that develop during the charge-discharge cycles better [29]. The discoveries of tin based amorphous oxide anode materials, the development of macroporous electrodes are significant. The multi-redox centered compound, LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (Ni$^{2+}$/Ni$^{3+}$) and LiFePO$_4$ appears to show much promise as cathode materials [30]. The need to increase the capacity and to maintain the high charge/discharge cycles would require systems that are electrochemically active and undergo redox changes that involve more than one electron. In the light of this, the Ni$^{2+}$→Ni$^{4+}$, and V$^{3+}$→V$^{5+}$ would offer considerable scope. It is also preferable to investigate other class of compounds such as nitrides, phosphides, intermetallics, etc. The cost of the battery could be an impediment to use many materials, unless the batteries are meant for specialized needs (medical, space and military related). Under the circumstances, the role of the materials chemist is important in this area of research.
4.3 Hydrogen storage materials

For hydrogen to be used as a viable fuel in fuel cells and other related technologies, suitable storage materials must be developed. The storage of hydrogen must take into account the many constraints such as weight, volume, efficiency, safety, cost, etc. Much focus and emphasis has been given to storing hydrogen in solids and accordingly solid state chemistry has a significant role in developing such materials. Hydrogen is, generally, taken up using adsorption (physisorption and chemisorption), absorption and chemical reaction mechanisms. Materials that possess large surface area (carbon nanotubes) offer excellent opportunities via the adsorption process, while hydride forming alloys (hydrogen stored in the interstitial sites) use absorption process and metal hydrides employ the chemical reaction pathways for the storage and release of hydrogen.

It has been shown that up to ∼5% hydrogen can be adsorbed on carbon nanotubes at 77K and about 1%, at room temperature [31]. The favourable van der Waals interactions between the adsorbed hydrogen and the internal surface for easy release of hydrogen might work against for adsorbing larger quantities at room temperature. Recent studies have shown that crystalline microporous metal-organic framework (MOF) compounds comprising metal ions or metal oxo clusters could provide a reasonable alternative. Hydrogen adsorption of up to 2–4 wt% has been observed at low temperature and high pressures [32].

Intermetallic compounds and alloys for hydrogen storage employs chemical cleaving of H2 bond at the surface and intercalating the atomic hydrogen in lattice interstitial sites [33]. The compound, LaNi5, can absorb one atom of hydrogen per metal atom at room temperature and 1–2 atm pressure forming LaNi5H6. Hydrogen can be released by heating the sample to temperatures <100°C. The uptake and release of hydrogen can be recycled and generally about 2 wt% can be adsorbed in these compounds. The main problem in utilising the intermetallics and alloys as hydrogen storage and transporting agent is their weight and cost. Other related alternatives would be to use the lighter elements (Li, Na, Mg, etc.) as constituents in intermetallics.

The light weight complex hydrides have been considered as a means of hydrogen storage by chemical reaction pathways. Thus, NaAlH4 and other related borohydrides are being studied. NaAlH4 contains AlH4 anions (alanate ion) with strong Al—H bonds and poses difficulties for the removal of hydrogen under normal conditions. The hydrogen can be released by heating the sample close to the melting point and recent studies reveal that the addition of Ti as the catalyst can bring down the temperature of release of hydrogen to about 180°C. Though these compounds can be possible candidates for hydrogen storage, much work needs to be carried out to understand and evaluate the dehydrogenation pathways, reducing the temperature of release of hydrogen etc. [34].

Another class of materials that has been investigated for possible hydrogen storage applications are the clathrate hydrates. Clathrate hydrates of methane have been studied as they were assumed to be present in vast quantities on the ocean floor, where the high pressures needed to stabilize the clathrates exist [35]. In gas hydrates, the water molecules usually form cages in which guest molecules, such as methane, could be trapped. It was discovered that hydrogen molecules can also be encapsulated in such clathrate structures, albeit at very high pressures (about 2 kbar). This precludes their practical application for hydrogen storage.

Recently, it has been shown that the pressure for storing hydrogen as gas hydrates could be significantly reduced by having THF (tetrahydrofuran) as co-occluding molecule (100 bar) [36]. In the class-II clathrate, the water molecules form two different sized cavities – the larger one with a free diameter of ∼0.67 nm and the smaller one ∼0.5 nm. For a clathrate to be stable, the large cages must be almost completely filled with suitable guest molecules, while the smaller cages may either remain empty or be filled with guest species. It has been shown that the larger cavity can be filled with tetrahydrofuran (THF) leaving the smaller sized cavities for storing hydrogen. Thus, with the use of binary clathrate hydrate, one can store up to ∼4 wt% of hydrogen. Clathrate hydrates are, thus, comparable to other systems discussed for hydrogen storage such as light metal hydrides and appear to be superior to cryosystems that use adsorbents with a large surface area.

4.4 Fuel cells

Fuel cell technologies are important as an alternative source of energy for the fossil fuel, reducing CO2 emission etc. [37,38]. The H2/O2 fuel cell requires good conducting membranes for proton and oxygen (electrolyte) and suitable electrodes for the reaction H2 → 2H+ + e− or O2 + 4e− → 2O22−. In addition a good electronic conductor would also be required for the delivery and removal of electrons. The direct methanol fuel cells (DMFCs) are not suitable due to the high cost of the catalyst (Pt) and possible issues related to the reactants and product crossover. Intermetallics such as PtBi and Ru doped Pt are being studied as alternate catalysts in DMFC [39]. Further work is needed to look for new type of catalysts which would also
reduce the overpotential at the cathode. Work on proton conductors or oxygen ion conductors are also being carried out. It is becoming clear that there are many interfaces to consider in materials that are required for use in fuel cells and also in high temperature electrochemical devices.

4.5 Photovoltaics

Polycrystalline thin film solar cells are important due to their high efficiencies and ease of preparation [40]. Thus, Cu(InGa)Se₂, CdTe and other semiconductors have been studied for photovoltaic behaviour with reasonable efficiencies. The high cost of the In and Ga along with the toxicity associated with Cd are reasons for not utilising them for harvesting the solar radiation. New solid state materials are needed that would have bang gaps in the range 1–1.7 eV. The development of such materials requires a deep understanding of the electronic structures, the bulk and surface dopant and defect chemistries along with contributions from theoretical calculations.

4.6 Luminescent materials

The ever increasing power requirements create opportunities for solid state materials chemists to investigate newer materials that could lead to greater efficiencies and energy savings in the generation and use of light. Mercury based fluorescent lamps represent one of the most efficient sources for lighting. The use of quantum splitting phosphors with quantum efficiencies more than 1 can be considered for lighting purposes [41]. To achieve quantum efficiencies of \( > 1 \), one needs to match the energy levels of absorption and emission processes along with observing the emission in the red, green and blue region of the visible light – a combination of these would give rise to white light. Solid state lighting is also being developed on the basis of LED-excited inorganic phosphors. Any development in this area requires a good understanding of the local crystal structure and the energy levels of the dopant ion.

Considerable effort has been expended on the development of organic light emitting devices (OLEDs), which function on the basis of favourable electron-hole combination processes. The development in this area is hindered by the lack of bright light and low life times (stability). The polycrystalline inorganic solid based light emitting devices (ILEDs) that work on the principles of OLED are being investigated due to the lower cost. A solid state ILED has not been realized yet due to the high work function (typically 8 eV) and high energy barriers for the hole injection in inorganic phosphors. Wide band gap inorganic luminescent materials with work functions of about 5 eV provide hope for realising ILEDs [42].

4.7 Transparent conductors

Transparent conductors that have both the optical transparency and electrical conductivity in the same material, are important for many applications such as automobile and airplane windows defrosters and transparent contacts for solar cells and displays. These are based on n-type oxides and the first example of transparent thin-film transistor (TTFT) is known only recently [43]. The main challenge in this area is to produce transparent conductors based on p-type materials that can be used in high performance complementary devices similar to silicon CMOS technology [44].

5. Creating materials – the role of chemistry [45]

The essence of research in chemistry is the synthesis, and it is also true for materials chemistry. If new compounds are not made, then the discovery of newer properties also cannot be found. Traditionally solid state materials are prepared by ceramic technique – by using the high temperature solid state reactions. Exploratory synthesis based on trial and error approach has yielded numerous discoveries and continues to be a valuable and popular method in the chemistry of materials. In this context, it is important to mention that India is very well placed due to the availability of large pool of trained manpower, which is an asset. Directed synthesis is generally employed to target a particular property. Trial and error methods and the directed synthesis approaches have provided reasonable advances in the area of materials science. Combinatorial, high throughput and parallel methods of syntheses allow for optimising experimental conditions and hold considerable promise. These approaches must be encouraged in India as they are relatively easy with low input costs.

In general, for the synthesis of a solid, in addition to the high temperature approach, synthesis from fluxes and melts, hydrothermal methods and also preparation from solutions have been employed. Recently, synthesis of extended framework compounds by directed assembly of molecular building blocks, low-temperature synthesis of oxides and chalcogenides in the nanometer sizes, are emerging as important developments. In spite of the considerable progress made, it is still a challenge to design and predict new phases \textit{a priori}. Considerable success has been achieved in the preparation of homologous series...
of compounds – in this approach the fundamental concepts that define the basic building units and how they combine are preserved but the major problem of decreasing stability and accessibility of higher homologues in a series still remains and requires attention.

5.1 High temperature synthesis

Synthesis at high temperatures involves reaction between the constituents at elevated temperatures and the reaction generally proceeds through the diffusion of the reactants. The low diffusion coefficients of the constituents in solid phases (in the order of $10^{-12}$ cm$^2$ s$^{-1}$) along with the requirement of high thermal activation barriers pose obstacles for the completion of the reaction. A prior knowledge of the phase diagram of the reactants would help in identifying suitable reaction conditions. In this process, the reactants, taken in stoichiometric quantities, are mixed thoroughly, pressed into a pellet and heated in a furnace at elevated temperatures. A problem associated with the high temperature synthesis is that monitoring of the progress of the reaction is difficult. It would also be difficult to separate phases, if mixtures of solids are formed during the reaction. To overcome such problems, researchers employ a variety of precursor techniques with the basic idea being to take the reactants in one single entity. In spite of all the shortcomings, the importance and use of the high temperature synthesis in materials chemistry cannot be understated. The synthesis of cuprate superconductors, the CMR manganates, dielectric semiconductors, half-metallic ferromagnets, etc. are examples of the versatility and success of the high temperature method.

5.2 Chimie douce/soft-chemistry methods [46,47]

High temperatures are often employed in ceramic synthesis in order to drive the reaction to completion, resulting in thermodynamically stable phases as products. This, however, is a major limitation because many of the interesting inorganic materials are metastable phases. Also, high temperature synthesis precludes realization of the products in the form of free-standing fine particles, nanoparticles and thin films. Synthesis of solids in fine particle/nanoparticle morphology as also thin films require special strategies that control particle growth of products during formation.

Metastable phases are better prepared by alternate synthesis routes based on a sound understanding of the chemistry behind synthesis, viz., thermodynamics, kinetics and reactivities in the solid state. The governing principle behind this approach, which is called chimie douce/soft chemistry methods is to have kinetic control rather than thermodynamic control, so that metastable phases could be accessed. There are several ways to achieve kinetic control of synthesis. One could, for example, prepare a thermodynamically stable phase by conventional means and subsequently transform it to a metastable phase through appropriate soft chemical reaction. For example, NASICON-framework phosphate, $V_2(PO_4)_3$, was prepared from $Na_3V_2(PO_4)_3$ by redox deintercalation of sodium using $Cl_2/Br_2$ in nonaqueous medium. It is also possible to obtain a metastable phase by carrying out the synthesis at conditions (e.g., high pressure, high temperature) at which the phase is thermodynamically stable and quenching it to laboratory conditions. The recent synthesis of ferromagnetic-ferroelectric $Bi_2NiMnO_6$ is an example. Accessing metastable phases through control of nucleation and growth kinetics in the presence of suitable templates under hydrothermal conditions is another well-known strategy that is commonly employed for the synthesis of zeolitic and microporous solids.

Among the several chimie douce approaches that have been developed to overcome the limitations of the conventional ceramic method, metathesis (chemical double exchange) is noteworthy [48]. Although metathesis reactions involving exchange of atomic/ionic entities between reaction partners for example, $Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$ (Thermite reaction) has long been known and even finds application (e.g. rail track welding), use of reactions of this kind for synthesis of inorganic materials in general is a development of recent times. The prime characteristic of such metathesis reactions is that they are highly exothermic, evolving a large amount of heat almost instantaneously. Some of the typical examples of metathesis reactions employed in the synthesis of non-oxide materials are:

$$\text{MoCl}_5 + 5/2(\text{Na}_2\text{S}) \rightarrow \text{MoS}_2 + 5\text{NaCl} + 1/2\text{S};$$

$$\Delta H = -890 \text{ kJ mol}^{-1}$$

$$\text{GaI}_3 + \text{Na}_3\text{As} \rightarrow \text{GaAs} + 3\text{NaI};$$

$$\Delta H = -489 \text{ kJ mol}^{-1}$$

$$\text{TiCl}_3 + \text{Li}_3\text{N} \rightarrow \text{TiN} + 3\text{LiCl};$$

$$\Delta H = -670 \text{ kJ mol}^{-1}$$

$$\text{GaCl}_3 + \text{Li}_3\text{N} \rightarrow \text{GaN} + 3\text{LiCl};$$

$$\Delta H = -645 \text{ kJ mol}^{-1}$$

The large reaction enthalpies result in high adiabatic reaction temperatures generally
Figure 6. The structure of (a) $K_2La_2Ti_3O_{10}$ and the metathetic modifications by the reaction with (b) BiOCl to form (c) $Bi_2La_2Ti_3O_{12}$ phase.

$>$1000°C, making the product formation almost instantaneous. While the high temperatures generated favour the formation of thermodynamically stable phases, the short reaction duration could in some cases stabilize metastable phases (e.g. cubic zirconia) in synthesis based on this approach.

A different kind of metathesis developed by one of us (JG) enables structural control during synthesis enabling formation of pre-determined products. A typical example is

$$K_2La_2Ti_3O_{10} + 2BiOCl \rightarrow [Bi_2O_2][La_2Ti_3O_{10}] + 2KCl$$

where a Ruddlesden–Popper phase is topochemically transformed into the corresponding Aurvillian phase. Here, the layered perovskite entity, $[La_2Ti_3O_{10}]^{2-}$ and the layered $[Bi_2O_2]^{3+}$ unit, which are exchanged retain their structural identity in the product (figure 6). Similar metatheses have been carried out with VOSO$_4$ and $Sr_2Cu_2O_2Cl_2$, instead of BiOCl, yielding novel metastable materials, $[VO][La_2Ti_3O_{10}]$ and $[Sr_2CuO_2][La_2Ti_3O_{10}]$, which are otherwise inaccessible by conventional means.

A major difference between metathesis reactions of this kind and those listed earlier is that these reactions are not self-propagating and requires longer duration. The formation of the co-produced ionic salt with a high lattice energy is likely the driving force for such reactions, but since the reaction enthalpies are not likely to be high, metathesis of this kind requires longer duration while stabilizing metastable products at relatively low temperatures. The combination of oxidizing and reducing agents in an appropriate manner to form controllable flame at relatively low temperatures through combustion has been fruitfully employed for the preparation of a variety of oxide materials with nanocrystallinity [49]. Though this approach is fast, the resulting product needs to be further processed at elevated temperatures to obtain good crystallinity.

6. Understanding materials – theoretical developments

The development of several methodologies during the last two decades along with the availability of powerful computers has contributed significantly towards the improvements in the theoretical investigations. The early electronic structure calculations based on local spin density approximation (LSDA) methods generally fails when
employed for strongly correlated systems such as transition metal oxides [50]. The realistic description of the electronic structure of magnetic systems containing strongly correlated localized electrons can be treated by a modified approach of using a combination of LSDA and Hubbard ‘U’ method (LSDA + U) [51] and the self-interaction corrected pseudo-potential method (pseudo-SIC) [52]. The two methods, though different, yield band gaps and band structures, magnetic moments and crystal structures that are in reasonable agreement with the experimental findings.

Recently, computer intensive methods, such as the LDA + DMFT and the GW, have been developed for more rigorous physical foundation. The developments of the first-principles description of strongly correlated materials along with the emergence of ‘theory of polarizations’ have helped in the conceptual understanding of spontaneous polarizations in bulk crystals (complicated by the periodicity of the crystal lattice) within the density functional framework [53]. These developments have helped in the calculations of ferroelectric polarizations, dielectric constants, piezoelectric coefficients and the electric field responses in a solid, routinely. The development of first principles method for calculating metal-insulator heterostructures is another important development. The advancements in the \textit{ab initio} methods will be very beneficial for understanding the electronic and structural study of solids.

The quantum density functional theoretical (DFT) methods, generally, are limited to 1000 atoms and \(\sim 10^{-12}\) s time scales and the tight binding methods are limited to < 10\(^9\) atoms. The use of classical interatomic potential help in simulating about million times larger size both in number (space) and time as such large systems are required to study the problems of interest in solid state chemistry. The growing use of molecular modeling (MM) in combination with the quantum mechanics (QM) could help in arriving at better results. The QM methods can be applied for studying the chemical reactions, the change of coordination numbers whereas MM methods can be applied for classical interactions. Thus, the QM-MM approaches would require careful consideration in the incorporation of QM methodology within the MM surroundings. By combining molecular dynamics (MD) with Monte-Carlo techniques employing the bond order dependent potentials, one is in a position to investigate the many issues associated with materials chemistry [54].

The theoretical advancements over the years have been employed in the areas of synthesis, in understanding phase stabilities in multi-component systems, kinetic studies, magnetic behavior, spin polarizations in complex solids, thermoelectrics and in multi-functional solids. The tremendous advancement in utilizing the density functional methodology along with the computational power, the electronic structure theory has now become an integral part of research in solid state chemistry. The electronic structure theory helps not only in the interpretation and rationalization of experimental results, but also in our understanding of the crystal structure-property relationships. It is important that the theoretical methods need to be developed from being an analytical tool into a more predictive instrument to make computationally designed materials. The DFT methods used for determining band gaps, elastic and other related properties may be improved to study a combination of properties via high throughput methods. Computational methods may be developed to study competing properties such as multiferroics and employed to suggest target compositions and structures for future synthesis. It is important to utilize the knowledge garnered from the synthesis along with the advancements obtained from computational approaches gainfully to meet the demands of the developing area of materials chemistry.

The need for more accurate band structure methods necessitates the development of more efficient algorithms [55]. The importance of interfacial interactions observed in quantum dots or nano-thermoelectrics with larger length scales require advancements in the DFT methods. The inability of the DFT to handle the van der Waals interactions and hydrogen bonds in solids is another area where developments are required. The non-local functionals, which are computationally intense, need improvements to describe many of the properties of layered solids such as graphite, MoS\(_2\), etc. Theoretical understanding of the electron transfer processes have not been developed in great detail and this is another area which requires attention. A major hurdle in the utilization of theoretical methodologies in solid state chemistry research is the lack of proper literature describing the usefulness of DFT and other techniques in a language accessible to non-experts. For a more elaborate account, the article by Kanatzidis and Poeppelmeier is recommended, which provides an excellent survey of the current research scenario (both experiment and theory) of this field with an international perspective [56].

7. Concluding remarks

A brief overview of the current scenario of materials chemistry presented here, \textit{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 a posteriori, what is required is theory with possible predictability. Of course, we do realize that it is a tall order for the field of chemistry [57], more so in the field of materials [58].

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