© *Proc. Indian natn. Sci. Acad.*, **52**, A, No. 1, 1986, pp. 1–24
Printed in India.

DEVELOPMENTS IN SOLID STATE CHEMISTRY : A PARTIAL OVERVIEW*+

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(*Received 4 December 1985*)

A brief survey of recent trends in solid state chemistry is presented. Some of the topics covered are crystal chemistry, synthesis, techniques of characterization, non-stoichiometry, phase transitions, reactions, structure-property relations, non-crystalline solids and catalysts. Several examples from the work carried out in the author's laboratory are cited.

INTRODUCTION

SOLID State Chemistry has emerged to become one of the important interface areas in modern chemical science. We cannot possibly forget that one of the earliest problems that intrigued chemists related to the stoichiometry of chemical compounds in the solid state. This age-old controversy between Bertholet and Proust whether compounds were stoichiometric or non-stoichiometric has been understood relatively recently. The periodic table has formed the basis for many of the advances made in solid state science. It is in efforts to simulate group IV elements like silicon and germanium that a large number of III-V, II-VI, I-VII compounds possessing a variety of electronic properties of technological value were investigated. Intelligent use of the periodic table continues to provide a wealth of ideas for preparing new types of solids possessing novel structures and properties. Solid state chemistry is gaining incaersing importance in the last few years because of its role in developing new materials as well as substitutes for natural materials.[1,2]

Chemical science may be considered to have three major components: structure, dynamics and synthesis. These three facets of chemistry also form the essential basis for the contributions that chemists make to the study of solids. The unusual skill with which chemists relate structures of compounds to their properties and synthesize (tailor-make) substances of desired properties makes their contributions to the study of solids unique. Solid state chemistry has, therefore, become an essential part of the broader discipline of materials science with chemists providing their own methods and approaches to the study of solids. In this presentation, I shall briefly survey some recent trends in solid state chemistry[1,2] in an attempt to illustrate the nature of the subject and to show how it works.

*Presented at the Golden Jubilee Symposium of the Indian National Science Accademy on Solid State Chemistry, held during December 4–6, 1985.

+Contribution No. 338 from the Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012.

Crystal Chemistry

Crystal chemistry forms the backbone of much of solid state chemistry. Crystal chemical principles provide the basis for visualising and predicting structures.[3–6] Based on an understanding of the structure and bonding in crystals, one can explain properties of complex solids but and synthesize them. A unique feature of many reactions in solid state is that they are governed by crystal chemistry or packing rather than by the usual rules of chemical reactivity. Although various types of crystal structures have been adequately described in the literature, there have been attempts in recent years to find new ways of describing structures e.g. on basis of reflection, rotation and such operations.[5,7] The role of non-bonded interactions in determining inorganic structures is being increasingly recognised.[8] Molecular orbital calculations within the extended Hückel framework are often carried out to explain relative stabilities of structures.[9,10]

While the structure and lattice energies of common ionic solids can be satisfactorily accounted for within the framework of the Born model, properties of partly covalent solids such as III-V and II-VI compounds can be understood by taking ionicity into account. Phillips' scale of ionicity is eminently useful in this regard.[11] Cohesive energies and other properties of organic solids are adequately described by making use of atom-atom potentials, the form due to Kitaigorodskii being especially successful.[12]

Empirical criteria have been derived for the overlap of cation-cation and cation-anion-cation orbitals on the basis of crystal structures to provide a unified picture of magnetic and electronic properties of oxides and other inorganic solids.[13,14] Conceptual phase diagrams have been constructed in terms of the transfer energy, b, or overlap integral (Fig. 1). A large overlap integral may be due to strong cation-cation or cation-anion-cation interaction; since b depends on the atomic separation, R, the occurrence of a transition from a localized to collective electron behaviour at $b=b_c$ implies existence of a critical distance, R_c, for the transition to occur. One electron energy diagrams are constructed by assuming the most probable hybridization of anionic and cationic orbitals and such diagrams are useful in understanding and predicting electronic and other properties of materials (Fig. 2).

Synthesis

The most common method employed to prepare solids[2,15–17] is the ceramic method generally involving repeated grinding and heating of reactant powders; many complex oxides are prepared in this manner. Sealed tube reactions are used to prepare chalcogenides. The ceramic method involves large diffusion distances for the reacting cations (upto 100,000Å). Some novel chemical methods of preparing solids have emerged recently and these generally involve low temperatures and often give high surface area products. Of these, the compound or the solid solution precursor method is noteworthy[18–20]; the method involves forming a compound or solid solution which would contain the required (two or more) cations in the proper

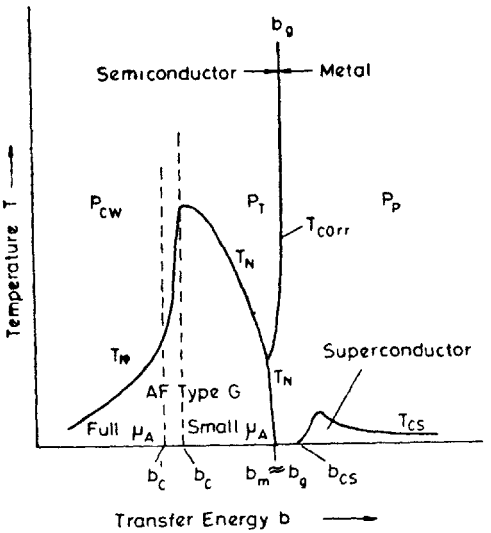

FIG 1 Schematic phase diagram[13,14]; n_i is the number of *d*-electrons per orbital.

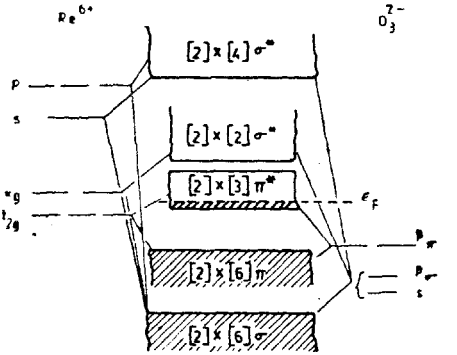

FIG 2 Schematic energy band scheme for ReO_3[13,14]

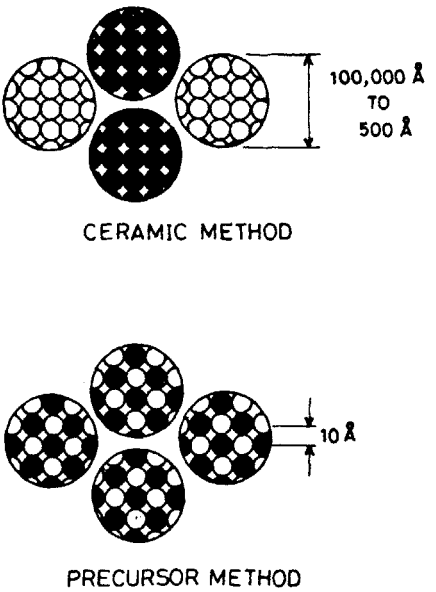

FIG 3 Distribution of different cations in reactant particles and the diffusion distances in (*a*) the ceramic method and (*b*) the precursor method.

ratio and having an anion lattice that can be readily modified or decomposed (Fig. 3). Since the cations are already mixed on an atomic scale (being hardly 10Å apart) in a single phase precursor, decomposition, oxidation or reduction is

rapid and complete at low temperatures. Compound precursors are not always easy to find for a required preparation. The solid solution method allows a continuous variation of the cation composition. Thus, by employing the carbonate precursor $Ca_{1-x}Mn_xCO_3$, one can make a variety of oxides in the Ca-Mn-O system; there are several other possible carbonate solid solutions of calcite structure formed by Ca, Cd, Mn, Fe and other metals. Unusual oxides such as $Ca_2Mn_{2-x}Fe_xO_5$ with novel metal coordinations have been prepared from precursors.[21] One can similarly employ nitrate, oxalate, cyanide and hydroxide precursors. Some oxides (e.g. $Pb_2Ru_{2-x}Pb_x^{4+}O_{7-y}$) can be made by synthesis in alkaline solution.[18] Intercalation, by chemical or elecrochemical means, gives oxides such as Li_xCoO_2, where Li^+ can be reversibly removed.

A number of solids such as transition metal chalcogenides, layered silicates and graphite have been used as host solids to intercalate guest species which vary from atomic species (hydrogen, alkali metals) to molecules (H_2O, NH_3, heterocyclics, organometallics). The subject of intercalation has grown enormously in the last five years.[22] The most well-known of the intercalation compounds are the different stage compounds of graphite with electron donor as well as acceptor guests (e.g. K, $FeCl_3$). Dichalcogenides of group IV, V and VI metals (Ti, Zr, Nb, Ta) possess layer structures which accommodate a variety of guest molecules including Lewis bases (e.g. amines), metal or molecular cations and neutral molecules. These intercalates show lattice expansion perpendicular to the layer planes and some of them exhibit superconductivity.

High pressures are often employed to stabilize high oxidation states of metals or to prepare oxides with a high degree of stoichiometry.[15] Hydrothermal conditions are conducive for preparing certain materials including quartz[23]. High temperatures often required to prepare refractory materials from melts are achieved by the arc method or the skull method.[17] The main point to note is that a broad range of conditions and unique ways of attaining them are available to solid state chemists today; these include irradiation by intense laser beams and electron beams, ultrarapid quenching, very high pressures, carefully controlled oxidising or reducing atmospheres and ultra-high vacuum. Such techniques combined with new methods of characterization have made it possible to prepare an astonishing variety of solids. In the family of metal oxides alone, over twenty homologous series of oxides have been discovered; besides oxides of different structures and controlled stoichiometries, novel suboxides of alkali metals, oxides formed by recurrent intergrowth and with infinitely adaptive structures have been discovered. Chemical vapour transport has provided a means of preparing a number of important materials.[4,17]

Techniques of Characterization

New and improved techniques of characterization that have become available in the last few years have revolutionized solid state chemistry. We shall briefly mention some of the important ones. While X-ray diffraction continues to be an indispensable tool for the determination of structure and identification, high resolution

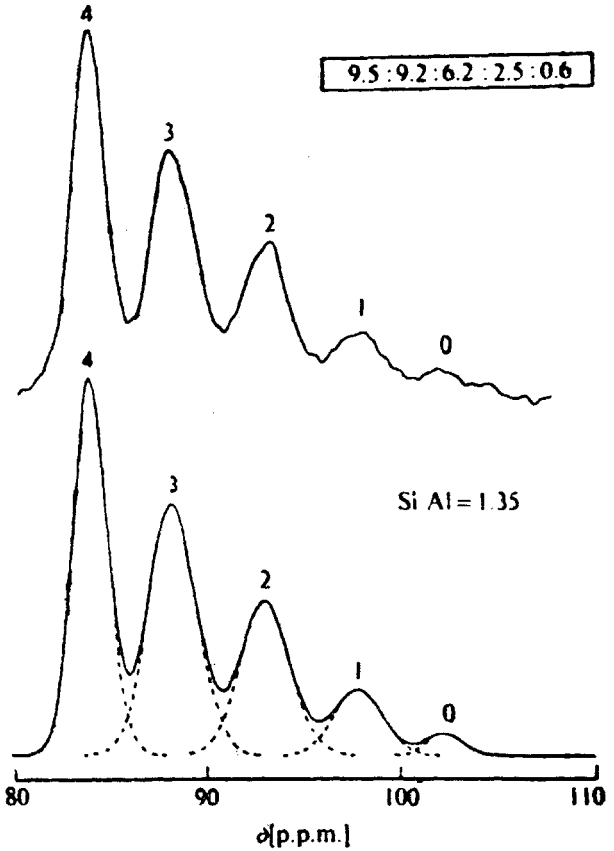

FIG 4 Magic angle spinning ^{29}Si NMR of faujasite : Observed (top) Simulated (bottom) Number shown on peaks are the number of Al atoms surrounding the Si atom.[26a]

transmission electron microscopy (HREM) has added a new dimension for investigating ultramicro structure and local order of solids; analytical electron microscopy (with EDAX and EELS) can be carried out on as little as 10^{-18} g of the sample.[24–26] Scanning transmission electron microscopy is used to study the morphology of particles (e.g. of catalysts) as small as 10Å. Electron diffraction which is an essential part of HREM provides information on superstructures resulting from defect ordering often not found by X-ray diffraction. Profile analysis of diffraction patterns (both neutron and X-ray) enables the study of structural details even with powder samples. The availability of intense neutron sources has made the neutron diffraction profile analysis[27] specially more powerful.

Structural tools such as neutron spectroscopy, optical spectroscopy and Mössbauer spectroscopy are well known.[2,4,17,23,28] A recent addition to the arsenal of solid state chemists is high resolution NMR spectroscopy of solids with magic angle spinning and cross polarization.[29,30] For example, the ordering of Al and Si

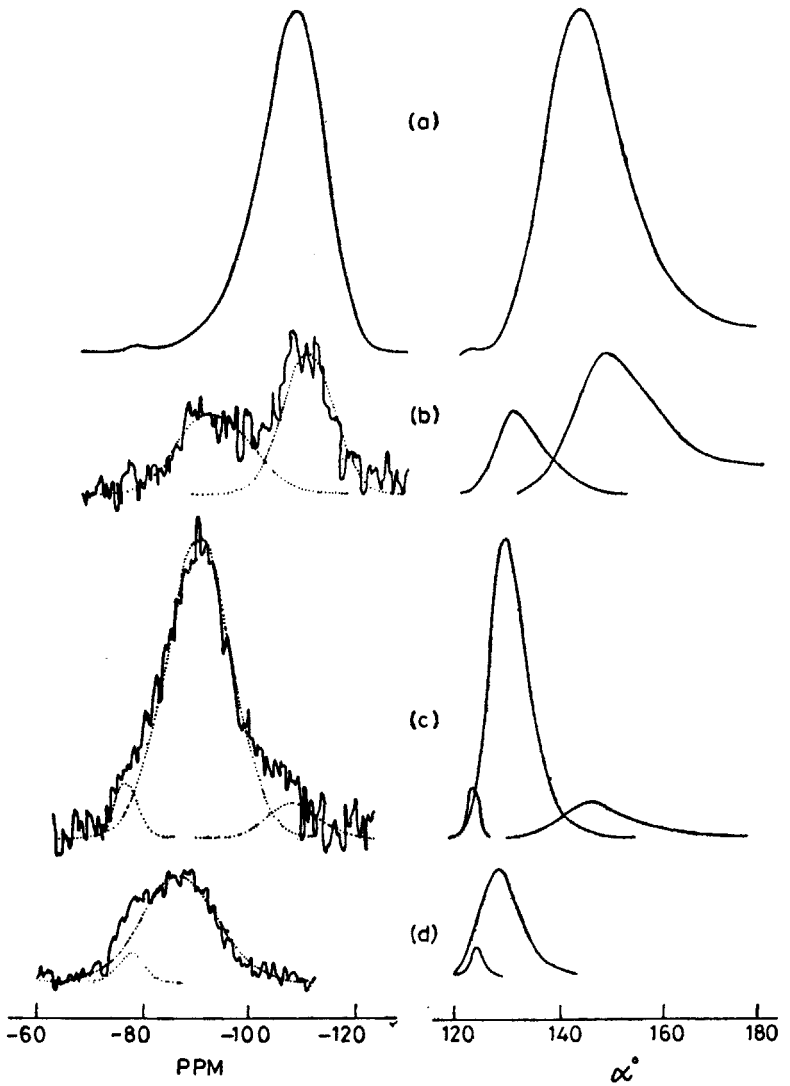

FIG 5 ^{29}Si MASNMR spectra of lithium silicate glasses and their decomposition into Gaussians both in chemical shifts and Si—O—Si angles (α) : (*a*) vitreous silica; (*b*) $15Li_2O$-85 SiO_2 glass, (*c*) $33.3Li_2O$-66.7 SiO_2 glass, (*d*) $40Li_2O$-60 SiO_2 glass.[31]

atoms in zeolites can only be found by this technique (Fig. 4) and X-ray diffraction is of limited use in this regard. In Fig. 5, we show how the ^{29}Si MASNMR spectra of lithium silicate glasses provide information on the distribution of Si-O-Si angles.[31]

EXAFS, particularly with synchrotron radiation, has been useful to investigate amorphous materials and catalysts.[32] In Fig. 6, we give a typical example of the use of EXAFS in the study of catalysts. Surface techniques such as UV and

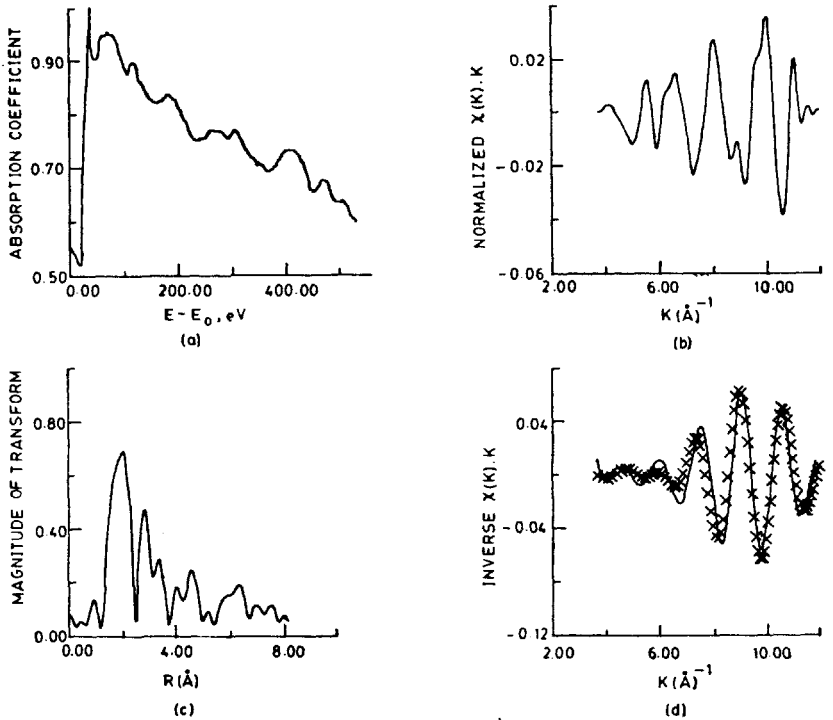

FIG 6 EXAFS study of Cu 75-Ni25/Al_2O_3 calalyst : (*a*) Raw EXAFS data; (*b*) normalized data; (*c*) Fourier transformed data; (*d*) back transform and fit to models (after Sankar, Vasudevan and Rao *unpublished results*).

X-ray photoelectron spectroscopy and Auger electron spectroscopy give direct information on the electron states of solids as well as on solid state phenomena.[33,34] What is truly gratifying today, is the variety of alternative techniques available for investigating solids. For example, the number of *d*-electron states in catalysts and other transition metal systems can be determined by Auger spectroscopy, X-ray absorption spectroscopy (EXAFS and XANES) and electron energy loss spectroscopy carried out in an electron microscope.[24,35,36] In Fig. 7, we show L edges of three transition metal oxides obtained from EELS carried out in an electron microscope.[24]

DEFECT SOLIDS AND NON-STOICHIOMETRY

Chemists have played a major role in the understanding of point defects in solids from the very beginning, the early contributions of Wagner being particularly noteworthy. Equlibria involving point defects have been usefully investigated from the quasichemical standpoint.[37] The essentials of the equlibrium treatment involve (*a*) the intrinsic equilibria of point defects and of electron distribution, (*b*) the ionization of defects, (*c*) the transfer reaction whereby atoms of the metal (cation) or the

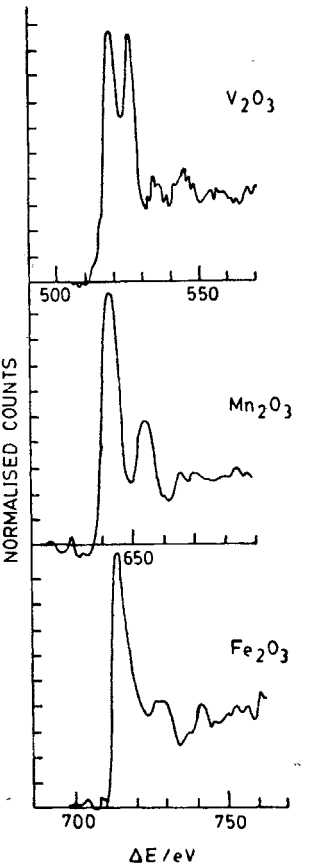

FIG 7 Metal L-absorption edges of three transition metal oxides obtained from EELS carried out in an electron microscope.[24]

ligand (anion) are exchanged between sites in the crystals and a gaseous phase at a given chemical potential in equilibrium with the crystal and (*d*) a charge balance condition. It was realized some years ago that all crystalline inorganic compounds have a finite composition range of stability and that it would be more appropriate to talk of the extent of non-stoichiometry in compounds rather than of non-stoichiometric compounds. Although the point defect model provided the basis for discussing non-stoichiometry and contributed much to the advances made in the area of defect solids,[38–40] newer concepts became necessary to understand systems with high defect concentrations.[41,42]

It has now become clear that in systems where deviations in the occupancy of cation and anion sites are large compared to the assigned crystal structure (say 0.1 to 20 per cent sites associated with vacancies or interstitials), the point defect model is not applicable. The real structure of such solids involves complexation or ordering of defects often giving rise to new structural ramifications.[41–46] Thus, in the well-known cation-deficient oxide FeO, defect complexes with four tetrahedral

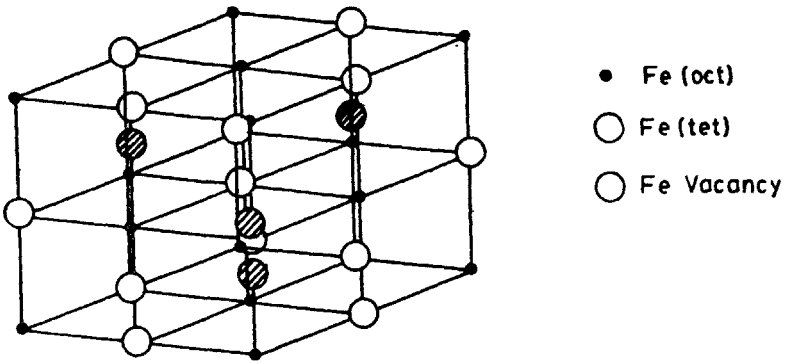

FIG 8 Koch-Cohen cluster in cation-deficient FeO.

iron atoms surrounded by 13 vacant sites (giving the ratio of octahedral cation vacancies to tetrahedral iron of 3.25) are present (Fig. 8). Defect complexes are found in anion-deficient oxides of fluorite structure. Such defect clusters are also found in Y_2O_3-YOF and in ZrO_2-Y_2O_3 systems. In anion excess flourites containing high defect concentrations, 2 : 2 : 2 clusters are found, a typical example being U_4O_9. In metallic TiO and NbO (with 15 per cent and 25 per cent of both cations and anions missing), defects are ordered giving rise to low-symmetry structures. Ordering of defects in such solids results in the formation of superstructures readily seen in electron diffraction patterns. A variety of solids show such superstructures including oxide perovskites, metal sulphides and carbides.[42,45] Computer calculations employing appropriate potentials which were once useful to investigate point defects are employed to study defect ordering as well.[38]

There are solids where the irrational anion : cation ratios are accommodated by the formation of planar defects or structural singularities. In anion-excess structures, (e.g., YF_3-YOF), interstitial atoms aggregate into an interstitial disc lying on a crystallographic orientation, the boundary climbing outwards until the singularity extends across the entire cross section of the crystal. In anion-deficient structures, anion vacancies aggregate into a vacancy disc of an appropriate orientation which undergoes a shear displacement until it extends across the crystal.[46] In this arrangement, cation coordination is preserved while the anion coordination is increased; the cation-cation distance is decreased because of the change from corner-sharing to edge-sharing or from edge-sharing to face-sharing of polyhedra. Such planar singularities eliminate a large number of point defects. If deviations from stoichiometry are large, the concentration of planar singularities becomes high and the singularities occur periodically giving rise to ordered phases with finite compositions. Across each planar singularity, slices of the parent structure are in proper register or in an antiphase relation with respect to the cation sublattice, the total composition of the crystal depending on the number of unit cells of the parent structure enclosed between two planar singularities. Creation of a crystallographic shear plane in ReO_3 type structures is shown schematically in Fig. 9. It is noteworthy

that even in very slightly reduced TiO_2 ($TiO_{1.9986}$), a number of shear planes are found, suggesting that even a very small departure from ideal stoichiometry creates shear structures rather than point defects. In the composition range $n = 9$–16 in Ti_nO_{2n-1}, there is a swinging of shear planes from (132) to (121) through (253), (374), (495) and so on.

In metal oxides derived from Nb_2O_5, intersecting shear planes occur giving rise to block structures. These structures respond in several ways to changes in metal-oxygen ratios. One shear plane may remain fixed while the other swings, giving rise to different cross-sections of the block, the block getting interconnected in different ways by means of edge- or face-sharing octahedra or tetrahedral sites. Block structures can accommodate a number of distinct compositions, typical ones being $Nb_{3n}O_{8n-3}$ and $Nb_{3n+1}O_{8n-2}$. Special mention must be made of the continuous series of ordered structures (having apparently irrational shear planes) or the so-called infinitely adaptive structures.[47] Examples of such structures are WO_3-Ta_2O_5 solid solutions and $Ba_p(Fe_2S_4)_q$.

There are several solids with large unit cells formed by recurrent intergrowth of two phases of similar structure but different compositions.[25] A typical class of such intergrowths is that of intergrowth tungsten bronzes.[48,49] An interesting class of intergrowth structures is the barium ferrite system, M_pY_q, where $M = BaFe_{12}O_{19}$ and $Y = Ba_2Me_2Fe_{12}O_{22}$ with Me = Zn, Co, Ni etc.[50] Another example is the family of intergrowth oxides of the formula $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$ formed[51] by oxides of the type $Bi_2A_{n-1}B_nO_{3n+3}$ (Fig. 10). None of the ordered or disordered intergrowth structures shows any evidence of vacancies or other point defects. Ordered and disordered intergrowth structures have been discussed recently.[52] It is truly remarkable that intergrowth structures are formed even though the component units can themselves exist as stable phases.

Phase Transitions

A variety of inorganic and organic solids exhibit transformations involving changes in crystal structure or electronic structure. On the basis of crystal chemistry, the nature of structural changes in phase transitions of simple solids can be predicted.[53,54] Besides nucleation-growth and order-disorder (both positional and orientational) transitions, martensitic transitions have also been observed in many inorganic solids. Polytypism is found in several inorganic solids including perovskite oxides.[54,54a] Of particular interest to chemists are phase transitions involving changes in the spin state of metal ions.[55] Several metal oxides and chalcogenides exhibit metal-insulator transitions induced by temperature, pressure or compositional changes (NiS, V_2O_3, $La_{1-x}Sr_xCoO_3$.[23,56–58] The transition in $LaCoO_3$ at 1200 K is interesting; it is believed that the *d*-electrons in $LaCoO_3$ which are localized at lower temperatures become itinerant after this phase transition, the entropy change at the transition being almost entirely electronic in origin. $Ag_{2+\delta}S$ and other silver chalcogenides become fast ion conductors due to melting of the cation sublattice at the transition temperature. The transitions are also accompanied by marked changes in electronic

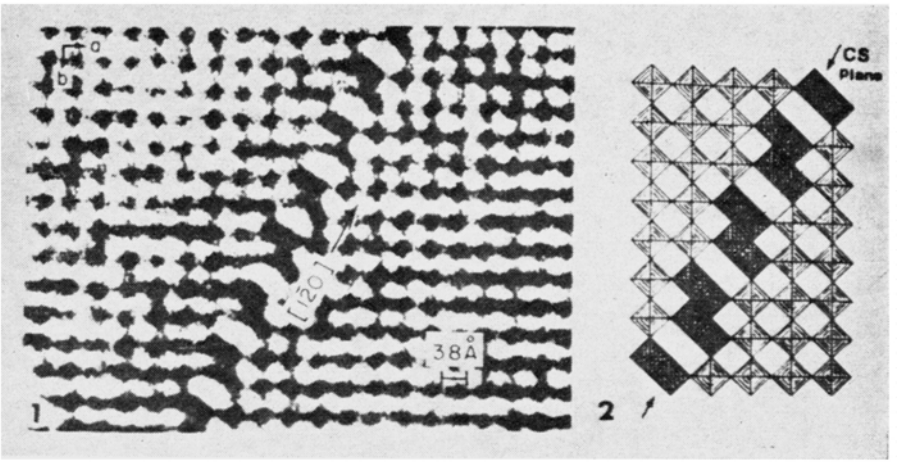

FIG 9 Crystallographic shear in WO_3; HREM image (1) and schematic drawing (2) are both shown.

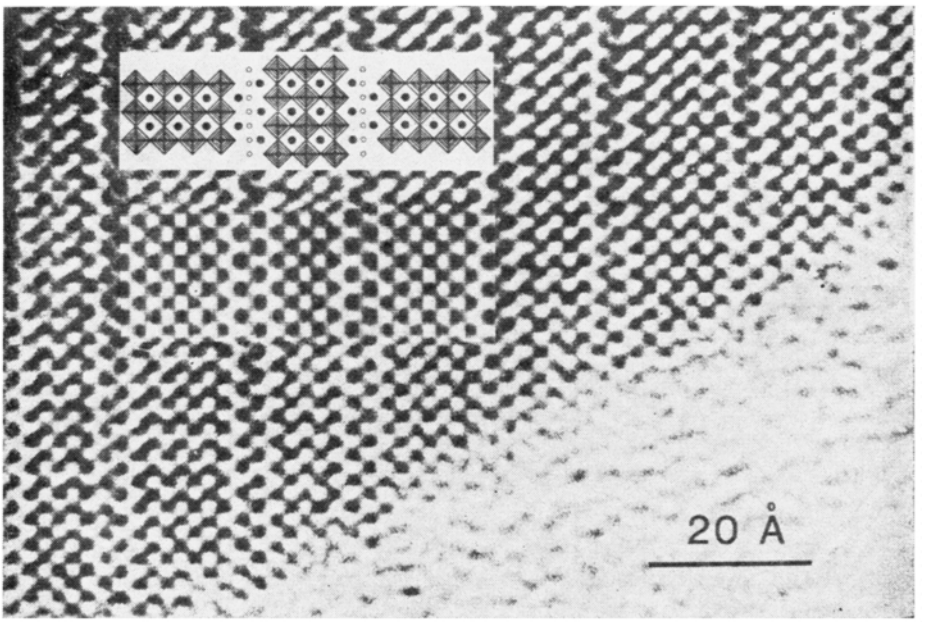

FIG 10 HREM image of $Bi_9Ti_6CrO_{27}$ formed by the recurrent intergrowth of $Bi_4Ti_3O_{12}$ and $Bi_5Ti_3CrO_{15}$. Computer-simulated image and structural drawing are also shown.[51]

conductivity; the nature as well as the magnitude of electronic conductivity is crucially controlled by stoichiometry.[59] A specially interesting metal-insulator transition is that induced by compositional changes (Fig. 11); it is noteworthy that

the value of conductivity at which the temperature coefficient changes sign corresponds to Mott's minimum metallic conductivity.[60]

Organic solids consisting of globular molecules become orientationally disordered (plastic) before they melt; the entropy of the crystal-plastic transition is considerably higher than that of fusion.[61,62] Several techniques are employed to study these transitions.

The subject of phase transitions is becoming increasingly an integral part of solid state chemistry and the changes in the physical properties of solids (magnetic, electrical, dielectric etc.) accompanying the transitions are not only of academic interest but also of technological relevance.[54]

A specially noteworthy advance made in the last 3 to 4 years is the computer simulation of phase transitions by Monte Carlo and molecular dynamics methods wherein variable-shape, variable-volume simulation cells are employed.[63,64] In Fig. 12 we show the results of a Monte Carlo simulation of the crystal to plastic state transition of CCl_4.

A recently recognized variety of phase transitions involves incommensurate structures resulting from two competing periodicities.[65,66] In conducting solids such as $TaSe_2$, interaction between electrons and ion cores occurs at low temperatures rendering the regular array of atoms unstable with respect to certain distortions. The stable state would be one where the charge density, the spin density or ion position exhibits long period modulations. The period of such modulations may be commensurate or incommensurate with the spacing of the underlying lattice. Such-electron-phonon coupled structural instabilities are known as charge density waves. Incommensurate structures in insulating solids such as $NaNO_2$ occur due to the presence of two transformations associated with order parameters of different symmetry. There has been increasing interest in modulated structures in solids.[67] Phase transitions of these solids and the so-called misfit structures[68] are undoubtedly of interest.

The origin of long-range-order in polytypes and related solids (e.g. recurrent intergrowth structures) is attracting some attention. The importance of infinite-range interaction and elastic forces has been pointed out[69,70]; an ANNI-type model is found to explain the occurrence of a variety of polytypes.[71]

Reactions

A variety of reactions occur in the solid state; decomposition of solids and oxidation and dehydration of solids are typical reactions which have been investigated in detail.[16] Intercalation reactions of solids was referred to earlier. Some solid state reactions exhibit topotactic or topochemical behaviour, typical examples being the oxidation of MnOOH and dehydration of brucite and α-AlOOH. Dehydration of $Mo_{1-x}W_xO_3$. H_2O to give oxides of ReO_3 structure is another example (Fig. 13). Many organic solid state reactions are also known to be topochemical.

Organic solid state reactions, especially those induced photochemically, are indeed interesting.[72] These reactions are mainly affected by molecular packing

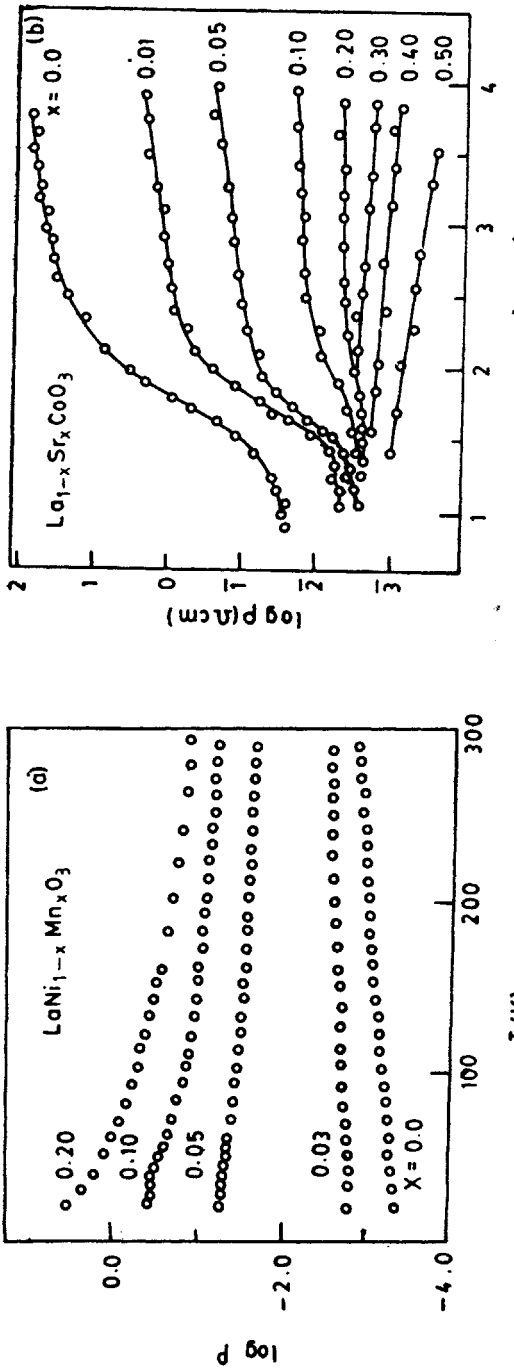

FIG 11 Compositionally induced metal-insulator transitions in $La_{1-x}Sr_xCoO_3$ and $LaNi_{1-x}Mn_xO_3$ (from the author's laboratory).

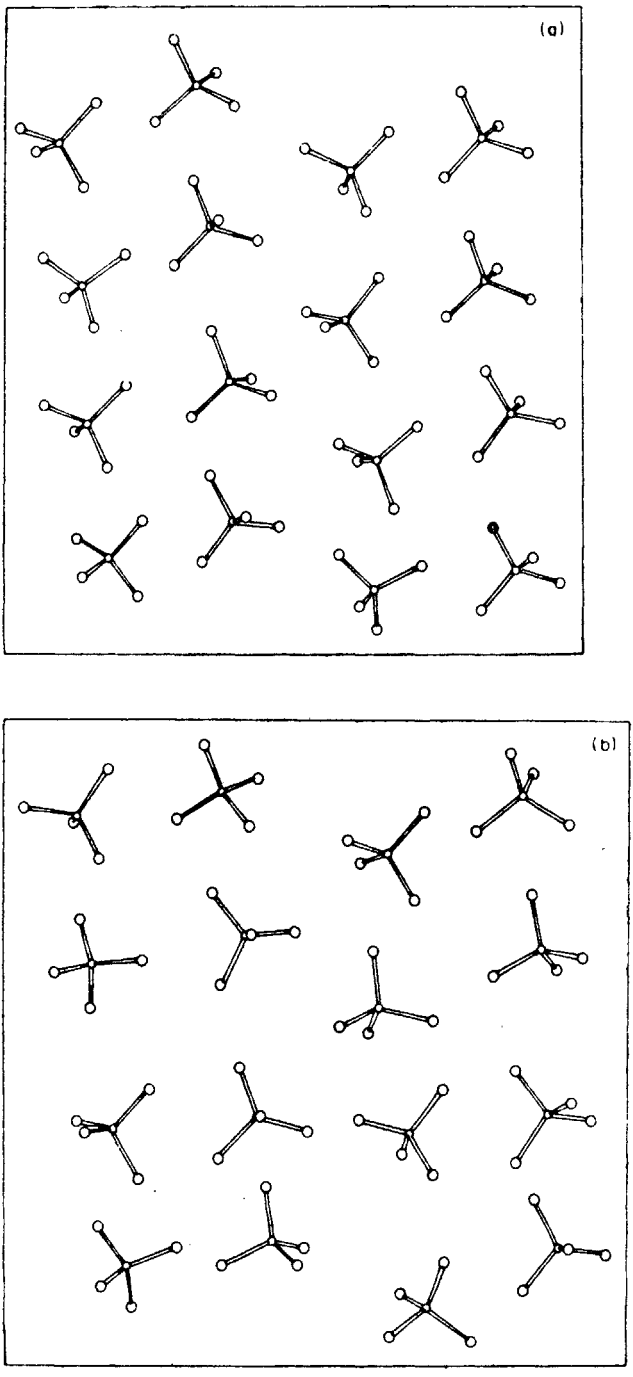

FIG 12 Monte Carlo simulation of CCl_4 at 1 GPa (*a*) crystalline phase at 380 K; (*b*) plastic (orientationally disordered) phase at 430 K.[64]

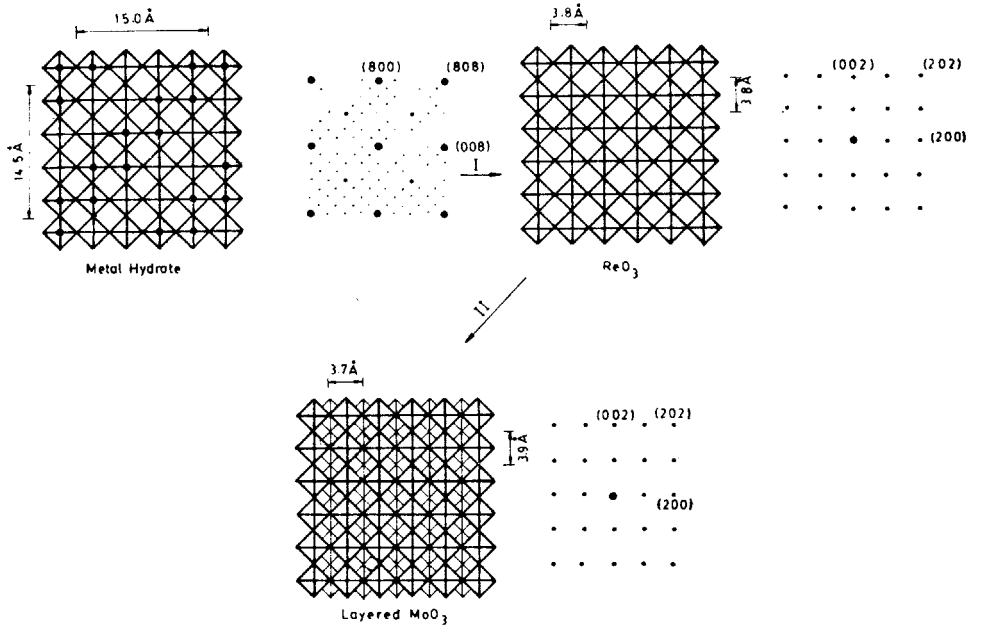

FIG 13 Schematic representation of the topotactic dehydration of the isostructural metal oxy hydrates, $Mo_{1-x}W_xO_3.H_2O$. ($0 \leqslant x \leqslant 1$) along with electron diffraction patterns. Dehydration yields $Mo_{1-x}W_xO_3$ of ReO_3-type structure. This is true even of $MoO_3.H_2O$ ($x = 0$), but the ReO_3 structure of MoO_3 is metable and transforms to the layered MoO_3 structure (*unpublished results from the author's laboratory*).

or by the presence of defects. The classic example of a reaction brought about by the proximity of the reactive centres in a solid is the photodimerization of trans-cinnamic acid where the α-form in which the molecules are packed with a head-to-tail relation yields the centrosymmetric truxillic acid dimer whereas the β-form with molecules packed in head-to-head relation gives the mirror symmetric truxinic acid; the γ-form in which the molecules are not favourably packed is photo-unreactive. Photodimerization of phenylbutadienes[73] investigated in this laboratory provides the possibility of a photochromic system, visible light dimerizing the butadiene and UV light reverting the dimer back to the diene (Fig. 14). Several types of solid state organic reactions have been described in the recent literature, of particular significance being those directed towards asymmetric synthesis.[74] It may not be long before the solid state route to organic synthesis comes into vogue on a routine basis (see articles of Jones and Thomas as well as Desiraju in this volume).

STRUCTURE-PROPERTY RELATIONS

Different classes of solids with wide ranges of properties have been investigated by solid state chemists in the last two decades. For example, oxides with metallic, semiconducting or insulator behaviour, ferro-, ferri-, antiferro- or para-magnetic behaviour and ferro-, antiferro- or para-electric behaviour have been explored.

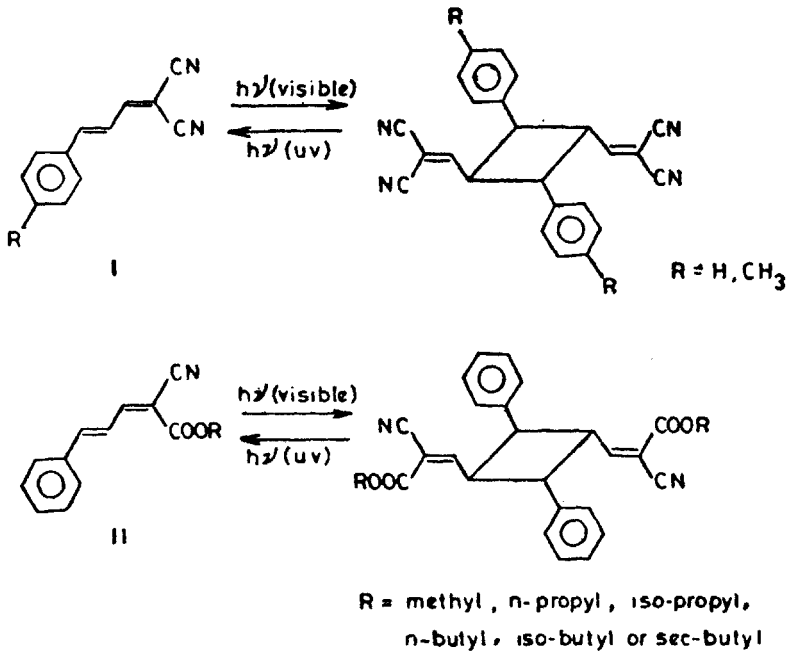

FIG 14 Photodimerization of phenylbutadienes in solid state.

Relating structure and properties of solids and making use of such relations for synthesising novel solids possessing desired properties forms an important mode of investigation of solid state chemists. Simple ion substitution, judiciously carried out, often results in remarkable changes in properties. For example, replacement of La by Sr in $LaCoO_3$[75] which is ordinarily a paramagnetic insulator results in metallic ferromagnets when the Sr concentration is above a critical value (*see* Fig. 11). Replacement of Si in Si_3N_4 partly by Al and N by O gives a new class of high-temperature ceramic materials called sialon.[76] Pressure effects can often be simulated by appropriate ion substitution; thus, the metal-insulator transition in V_2O_3 is shifted to lower temperatures on substitution of V by Ti (< 5 per cent) and the effect is similar to that obtained at high pressures. Substitution of V by Cr (< 1 per cent) produces a negative pressure effect. SmS shows a semiconductor-metal transition on application of pressure due to promotion of a $4f$ electron to the conduction band (valence fluctuation). Substitution of Sm by Gd (18 per cent) gives the high pressure metallic phase which on cooling explosively transforms to the semiconducting phase. Design of solid electrolytes (fast ion conductors) for possible application in energy devices is also made on the basis of structural considerations.

Electrical and magnetic properties of low-dimensional solids have attracted much attention in recent years,[77–79] some of the motivation resulting from the desire to make high temperature superconductors. Important organic conductors being

investigated are tetrathiofulvalene (TTF)—tetracyano-quinodimethane (TCNQ) and related charge-transfer solids and polyacetylene and related polymeric one-dimensional organic materials. By suitably doping polyacetylene, both *n*- and *p*-type semiconductors can be prepared. Amongst the inorganic one-dimensional conductors, $K_2Pt(CN)_4Br_{0.3}3H_2O$ (KCP) and related derivatives and Hg-chain compounds of the type $Hg_{3-\delta}AsF_6$ are noteworthy. Polymeric $(SN)_x$ becomes superconducting at very low temperatures.

Low dimensional solids have been employed as model magnetic systems, solids of K_2NiF_4 structure being typical two-dimensional materials which have been explored extensively. Structure and properties of oxides of K_2NiF_4 structure have been discussed in detail.[80] La_2NiO_4 has been found to show a metal-insulator transition in the *ab* plane with some evidence for antiferromagnetic ordering in this plane.[81] Low-dimensional solids containing both organic and inorganic groupings have been synthesized.

There is an entire class of materials called the ferroics (Fig. 15) where the orientation state is altered from one to another by application of one or more appropriate forces.[82] In a ferroelectric like $BaTiO_3$, the orientation state of spontaneous electrical polarization can be altered by the application of an electric field while in a ferromagnet such as CrO_2, the orientation state of spontaneous magnetization in domains is switched by the application of a magnetic field. In a ferroelastic such

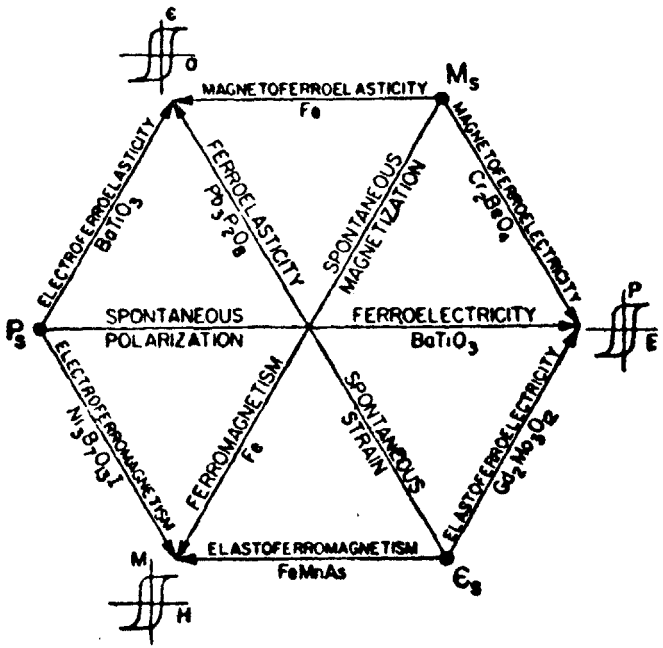

FIG 15 Diagram illustrating various types of order parameters involved in proper and improper ferroics.[82]

as $CaAl_2Si_2O_8$ the direction of spontaneous strain in a domain can be switched by the application of mechanical stress. Besides these three primary ferroics, we have secondary ferroics where orientations differ in derivative quantities like dielectric or magnetic susceptibility which characterize the induced effects. Ferrobielectric $SrTiO_3$, ferrobimagnetic NiO and ferrobielastic SiO_2 are examples of secondary ferroics. Induced effects can also result from cross coupled effects such as stress-induced polarization or magnetization (e.g., piezoelectricity and piezomagnetism). A combined effect of any two types of fields (e.g., elastoelectric or elastomagnetic effects) can also cause induced effects. A novel type of ferroics of technological value is that formed by composites made from ferroelectric ceramics and plastics.

Research in solid state ionics has become a major thrust area in the last few years because of its direct relevance to energy devices. Several materials exhibiting high ionic conductivity and little or no electronic conductivity have been prepared,[83,84] the oldest example being $Zr_{0\cdot85}Ca_{0\cdot15}O_{1\cdot85}$; this mixed oxide has found several technological applications. Some of the important superionic conductors are AgI related materials such $RbAg_4I_5$ and β-alumina ($Na_2O.11Al_2O_3$) and its analogues. β-alumina and similar sodium ion conductors could indeed find major applications in the sodium-sulphur battery. Other types of superionic conductors where the mobile ions are protons, Li^+, Na^+ and F^- have been discovered and there is the expectation that solid state ionics may make an impact through their use in advanced battery systems.

Efforts are underway in many laboratories to explore new systems for ion transport; based on structural considerations, several channel frameworks have been investigated, one of the interesting structures being $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ (NASICON). Although there has been considerable effort to investigate NASICON related structures, it appears that there is some uncertainty as to the exact composition of NASICON itself. Lithium ion conduction is also being examined for possible use in batteries. An interesting lithium ion conductor discovered recently is the Zintl alloy, LiAl. In this connection, the recent discovery of a rechargeable lightweight battery involving $LiClO_4$ and active carbon (open circuit voltage, 3.9V) is of much interest. A variety of challenging problems are being widely pursued by solid state chemists in the area of batteries and fuel cells. We are yet to find good low-cost oxygen electrodes for use in metal-air batteries and fuel cells; better electrocatalysts are to be found to make this possible. No specific guidelines for the choice of electrocatalysts are available, but high electronic conductivity and oxygen non-stoichiometry seem to be essential. Photoelectrochemical production of hydrogen[85] poses many problems where solid state chemists are making much contribution. Photovoltaic conversion of solar energy has been a major area of R and D with considerable success and promise.

There are many other classes of important materials with properties of academic as well as technological interest. Mixed valence systems,[86] liquid crystals and a variety of organic, ceramic and magnetic materials are some of them. For purpose of brevity, we shall not discuss these solids here.

Non Crystalline State

The amorphous state[87–89] has been recognized as one of great importance by physicists, electronic engineers and others but chemists seem to have neglected this area at least in the early stages. A large variety of materials of vital importance are amorphous or quasi-crystalline. For example, many of the catalyst preparations involve metals supported on amorphous or partially crystalline substrates while some of the materials used in photovoltaics are amorphous as are the active materials used in reprography and photography. High resolution electron microscopy has been used to delineate ultrastructural characteristics of microcrystalline, partially crystalline and amorphous silica and such studies are useful in providing operational criteria for making such distinctions. It is not possible however, to define a ground state for amorphous materials. Obviously, there can be degrees of amorphousness of a substance and we are yet to find out ways of quantifying the amorphous character of a substance and relate its origin and variations to structure and bonding. EXAFS and XANES have been used extensively to investigate structures of amorphous materials, but these techniques are not entirely fool-proof or always successful.

Most substances can be made amorphous by quenching melts or depositing vapours. Two important characteristics of the amorphous state are freedom from order and from compositional restrictions. Compositions of amorphous materials are continuously variable; because of this property, there is local saturation of valence requirements in covalently bonded solids or creation of structural groupings which achieve electrical neutrality in ionic systems. Amorphous materials exhibit unique electronic and other properties, some of which are of potential technological value. Glasses are amorphous but are distinct from other amorphous materials by virtue of the glass transition they exhibit. Although glasses are supposed to be in a metastable state, they exist as stable materials for indefinite periods. For example, vitreous carbon is employed in high temperature applications; crystallization of vitreous B_2O_3 is possible only under severe conditions.

In the last decade, there has been considerable activity in the area of amorphous solids in order to explore the physical laws that govern the behaviour of non-crystalline solids as well as to prepare new amorphous materials with controlled properties. A variety of amorphous solids including metallic glasses have been prepared. The quenching rates attainable today in melt-quenching techniques are of the order of 10^6–10^7 deg. sec^{-1}. We have available today, glasses with transparency in any region of the electromagnetic spectrum, glasses which are semiconducting or ferroelectric, glasses with controlled magnetic properties and so on. A great advantage of amorphous (and glassy) materials is the ease of fabrication.

The unique phenomenon of the glass transition[90] exhibited by glasses is a transition from one metastable, non-crystalline, rigid state to another metastable, non-crystalline, but non-rigid state characterized by features of pseudo second-order transitions. However, there is no totally satisfactory model or theory for this phenomenon. Some workers attach significance to a thermodynamic transition

temperature, T_0, where dynamic rates vanish, but this approach does not explain all the known properties of glasses. Results from computer simulation studies reveal the formation of clusters in supercooled liquids prior to glass transition. The glass transition could then be a congelation of these clusters. Clusters of 500–100Å diameter present in the non-crystalline intercluster tissue material of lower density, melt at the glass transition and add on to the volume of the tissue material. The recent Monte Carlo study of the glass transition in isopentane[64] has revealed the importance of geometric factors; the study depicts differences in packing and structure between the liquid and the glassy states.

A remarkable feature of amorphous solids governed by the chemistry of these materials is the occurrence of novel chemical transformations and structural rearrangements on an atomic scale. Thus, a continuous variation of the concentration of tetrahedral and planar (3-coordinated) borons is achieved in borate glasses by modifier oxides. Both over- and under-coordinated, charged chalcogen (or pnicogen) defect centres present in chalcogenide (and pnictide) glasses play a crucial role in transport and related properties. These charged pairs result from a favourable reaction of bonds which initially suffer homopolar scission. Oxygen coordination of germanium varies as a function of the modifier oxide in germania glass, varying from four to six and to four again in modifier oxide rich regions.

The nature of bonding in amorphous materials provides new challenges. As mentioned earlier, an important characteristic of the amorphous state is the presence of both compositional and density fluctuations; these fluctuations are accompanied by fluctuations in the nature of bonding. Most of the common multi-component oxide glasses consists of both charged ionically bonded oxygens and two-coordinated covalently bonded oxygens, their relative propertions being continuously variable. Chalcogenide glasses (e.g. As_2Se_3—As_2Te_3) are cases where both ionic and covalent bonds are present between similar sets of atoms.

A significant development in glasses is the observation of fast ion conduction.[90a] A variety of fast ion conducting glasses based on Ag^+ and Li^+ ions have been characterized. Besides the ease of fabrication, glassy fast ion conductors offer advantages of property manipulation through composition control. The field of optical communication is based on the development of glass fibres with controlled optical properties. A unique property of the glassy state is that the refractive index is determined by the chemistry of the glassy state; halide glasses offer tremendous possibilities in this direction. Unusual photostructural effects have been found in amorphous WSe_2 and other systems and it is of much interest to find out the cause of such effects and also their possible applications.

Recent studies[90] have shown that one can generate orientationally disordered glasses by quenching plastic crystals; these glasses also show a glass transition. Dipoles doped in ionic crystals (so called dipolar glasses) are also found to show a glass transition. These systems are indeed most interesting and show how the glass transition is not a property of positionally disordered glasses alone.

Recently, quasicrystalline alloys (e.g, Al-14 percent Mn) prepared by rapid solidification of melts have been found to exhibit three-dimensional icosahedral

point symmetry[91,92] or Penrose patterns. This was considered to be a revolution in crystallography, but Pauling's idea[93] based on chemical considerations suggest twinning of cubic crystals may be on important factor, but features such as the electron differation patterns are yet to be explained.

CATALYSTS

Modern chemical industry depends heavily on the development of appropriate catalysts. The performance of catalysts depends both on their solid state (bulk) and surface properties. Molybdate catalysts for olefin oxidation and ammoxidation reactions and shape-selective zeolites for various purposes (especially in petroleum industry, e.g. ZSM-5 for methanol to gasoline conversion) are typical examples of the new generation of catalysts. Design of shape-selective catalysts wherein the pore aperture and diffusion path lengths are finely engineered is an important aspect of catalyst development. Better catalysts are required for many reactions such as ammonia synthesis, hydrocarbon oxidation, methanol synthesis and for (Zeigler-Natta type) stereospecific reactions. It may be possible to use oxide catalysts such as defect perovskite oxides, supported V_2O_5 or molybdates for hydrocarbon oxidation, just as defective Cu/ZnO may be useful for methanol synthesis. Search for newer and better catalysts will undoubtedly continue. With the availability of new and improved techniques for the characterisation of the bulk and surface properties of solids, it is expected that the art of catalysis may soon become a science. Catalysts are accordingly included under solid state chemistry and materials science in recent years.[94] For example, the surface species on Co–Mo hydrodesulphurization catalysts is recently found to be of the type $CoMo_{2n}$ $(2n + 3)\ S_2^{2-} - (2n - 2)\ S^{2-}$, involving disulphide ions; this has been possible because of the use of X-ray photoelectron spectroscopy and X-ray absorption spectroscopy.[95] Besides photoelectron spectroscopy and related surface techniques, techniques such as NMR spectroscopy.[29,96] EXAFS[32] (see Fig. 6) and other techniques have proved to be a boon to the study of catalysts; FTIR spectroscopy seems to be ideally suited for study of molecular species on catalyst surfaces, especially when it is used in the reflection-absorption mode along with photoacoustic detection.

Metal cluster compounds containing metal aggregates surrounded by ligands provide model systems which simulate surface species produced by the interaction of molecules with metal surfaces.[97,98] Metal clusters may be considered to fall in the range of aggregation between single, mononuclear complexes and macroscopic crystallites, the latter including supported metal catalysts (e.g. Pt/Al_2O_3) which generally consist of aggregates of metal atoms (crystallites) bonded to an inert support. The support also contributes to catalytic effects in certain systems (e.g. Pt/TiO_2).

Metal cluster compounds are a combined outcome of efforts in organometallic chemistry, surface science, heterogeneous catalysis and allied fields. The development of selective catalysts for the C_1 chemical industry employing carbon monoxide (or possibly CO_2) as the raw material has resulted in major efforts in metal cluster research. The interest of solid state chemists and surface chemists in this area

arises from the close correspondence between metal cluster compounds and the metal crystallites on surfaces of supported metal catalysts as well as the surface species formed by molecules on catalyst (or metal) surfaces.

ACKNOWLEDGEMENTS

The author would like to acknowledge the support of the Department of Science and Technology, Government of India, and the University Grants Commission for support of his research in Solid State Chemistry.

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