© *Proc. Indian natn. Sci. Acad.*, **52**, A, No. 1, 1986, pp. 176–191.
Printed in India.

CHEMICAL BOND AND THE NATURE OF INORGANIC GLASSES*+

K J RAO

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

(*Received 4 December 1985*)

Bonding in inorganic glasses is generally a mixed ionic-covalent type. In highly ionic glasses intermediate range order develops with the formation of clusters. In covalently bonded glasses, formation of charged defects plays a significant role in many glass properties. Covalency itself appears to increase in the glassy state. In this article, examples of the consequences of the type bonding on the structure and stability of glasses have been presented. Inherent glass-forming tendency in several inorganic compounds is also discussed in the light of a chemical model.

Key Words : Chemical Bond; Inorganic Glasses; Intermediate Range Order; Covalency; Octahedral Motifs

INTRODUCTION

A number of inorganic systems are known to form glasses.[1–3] They are generally characterized by overwhelming chemical and structural complexity and elucidation of general principles governing to glassy state is not easy. There are, however, several chemically simple materials also which easily vitrify; for example, simple elements like S and Se, oxides like B_2O_3, SiO_2 and P_2O_5, chalcogenides like As_2S_3 and As_2Se_3 and halides like BeF_2 and $ZnCl_2$. They are mostly covalently bonded and considered to possess good glass-forming tendency. A similar tendency to vitrify is not prevalent among simple ionic metarials. Even the simplest ionic glasses are typified by those formed in binary nitrates, KNO_3–$Ca(NO_3)_2$ and sulphates K_2SO_4–$ZnSO_4$ and are fairly complex.[4–6] Further, glasses are formed only in certain restricted composition regimes with relative ease. It is common practice in glass literature to use descriptions like glass formers; glass-forming tendency etc. Such terms, although quite generally understood, are rather non-quantitative in the real sense. We have assumed for the present purpose that melts which vitrify with cooling rates not greater than 1000deg/sec are good glass formers.

There is thus an apparently strong influence of the nature of bonding on the vitrification of the materials. In our investigations of a number of inorganic glass systems, a few important features revealing the relation of bonding to the structure

*Contribution No. 343 from the Solid State and Structural Chemistry Unit.

+Presented at the INSA Golden Jubilee Symposium on Solid State Chemistry held at INSA, New Delhi during December 4–6, 1985.

and properties of glasses have been noted. These features have been discussed particularly in the context of some of the problems of the glassy state such as inherent glass-forming tendency in some materials.

Inorganic Glasses and Cluster Formation

Typical ionic glasses are formed in mixed sulphates K_2SO_4–Na_2SO_4–$ZnSO_4$ and in AgI–Ag_2MoO_4; the latter is an example of a fast ion conducting glass.[7,7a] They all contain discrete anions like SO_4^{2-} and MoO_4^{2-}. An important feature of ionic glasses is that the interaction is through non-directional and long-range coulombic forces. The long-range nature of the interactions in some way appears to induce nucleaction of ordered crystalline regions. It, therefore, makes it almost impossible to quench simple ionic melts like NaCl into glasses. In quenching binary or ternary melts advantage is taken of the fact that long-range diffusion required for growth of large crystallites of stable crystalline phases does not occur in the time-scale of cooling kinetics. Ionic glasses so obtained can be modelled using cluster model in which a glass is assumed to possess a cluster-tissue texture. Clusters would correspond to highly ordered, essentially crystalline regions whose spatial extension of 10–100 Å. Material present in the inter-cluster region is assumed to be truly amorphous and described as connective 'tissue' which possesses somewhat lower density. Normally the tissue is either enriched or impoverished compositionally though to a small degree with respect to atleast one mobile ionic species.[8–10]

Presence of fine clusters with crystalline order has been indirectly evidenced in AgI–Ag_2MoO_4 glasses.[11,12] But it is not essential that clusters should possess only a crystalline order. High degree of positional correlation of the ions is sufficient to describe it as a cluster. Such clusters called 'amorphons' could result from restrictions of ionic packing also. In sulphate glasses where a modified random packing model was found to serve as an adequate structural model, Zn^{2+} ions are coordinated always to six oxygen ions from six SO_4^{2-} ions in an octahedral geometry while K^+ and Na^+ ions are coordinated to 12 and 8 oxygens respectively from 4 sorrounding SO_4^{2-} ions.[4–6] Structures built with such features are unlikely to develop crystalline clusters with uniform composition. It may result in the formation of amorphons. Within the amorphon positional correlation of ions is very high. Amorphon clusters would be held together by disordered tissue-region of slightly lower density and again a cluster-tissue texture would ensue.

The presence of discrete anions and cations interacting coulombically would therefore give rise to a cluster-tissue texturing on an extremely fine scale. Formation of clusters in a variety of glasses (including ionic glasses) has been evidenced in many experiments. For example, in highly modified silicate glasses[13] and metallic glasses[14] fringe patterns have been observed in high resolution electron microscopy suggesting presence of highly ordered regions. Freezing of the spin-spin correlation times prior to thermal glass transition upon cooling of glass-forming

melts doped with tempone has been noted in ESR experiments in organic glasses,[15] suggesting formation of clusters in supercooled liquids prior to the incidence of glass transition. Evolution of roto-diffusive motions of sulphate ions in the tissue and on the cluster surfaces at a temperature below the thermal glass-transition while heating the samples has been noted in IR spectroscopy.[16] The pressure has been found to transform the tissue into clusters leading to total crystallization resulting in the expected conductivity changes in AgI–Ag_2O–MoO_3 glasses.[11,12] The high pressure studies have provided a remarkably unique evidence for the presence of clusters. A large number of direct and indirect evidences with regard to clustering in a variety of glass systems have been discussed by Phillips.[17]

The cluster tissue texture may thus be assumed to be a common feature of all ionic glasses. The cluster-tissue texture may inherit both density and compositional differences between the two regions. Cluster model has been treated quantitatively in order to investigate glass-transition phenomenon.[8,10]

Glass-transition itself is a characteristic thermal event occurring in glasses at a temperature which is roughly about 2/3 of the liquidus (or melting) temperature of the corresponding crystalline phase.[18,19] The transition in most real glasses is diffuse in comparison to solid-solid phase transitions in crystalline materials. However, step like changes occur in heat capacities and thermal expansivities which often give the impression that the underlying phenomenon shares features of a second order transformation.[20] The problem of glass-transition in the cluster model is addressed via its vibrational properties.[10] The less dense, disordered, tissue region is assumed to be characterized by highly anharmonic potential wells. As a result, potential energy wells coalesce at higher vibrational levels. Correspondingly, systematic increases occur in amplitudes along with decreased energy separations. At sufficiently high potential energy levels, the amplitudes and times of oscillations become very large and any uncorrelated random displacement in the neighbourhood can wipe out the memory of the vibrating species. Hence, a vibrational mode is converted into a translational mode. The occupancy of vibrational levels is a function of temperature. With increasing temperature, particles in ground vibrational state are excited to higher levels and the loss of particles from the ground vibrational state is replenished from the surfaces of the clusters which share features of anharmonicity on the side of the tissue. In other words, as the temperature is increased, particles in the tissue regions are excited to large amplitude states in coalesced potential wells providing for smooth evolution of translational modes from vibrational modes. This is followed by a continuous 'turning in' of particles from the cluster surfaces into the cauldron of the tissue, whose volume increases at the expense of the shrinking clusters. The rate of shrinking and thus the rate of the whole process increses rapidly towards the end when the clusters disappear, terminating in the glass transition.

With very few and plausible assumptions, this model has been used to show that

$$\xi = a^{1/3}\left[1 - \frac{(a-1)Z}{a}\right]^{1/3},$$

where $\xi = (\bar{r}_c^T / \bar{r}_c^0 = [\langle V_c^T \rangle / \langle V_c^0 \rangle]^{1/3}$

represent the ratio of the average radius of the cluster at temperature T to its average radius at $0K$, a is equal to the ratio of the total volume of glass to the total volume of the cluster at $0K$ and Z is the relevant partition function for the tissue region. ξ has been found to behave like an order parameter decreasing rapidly towards the glass-transition temperature, T_g. Hence, it would be profitable to associate ξ with the notion of a coherence length of a phonon mode so that in the reverse direction (while cooling) the glass transition exhibits a divergence in ξ producing the likeness of a mean field governed transition (Fig. 1).

Employing heuristic but plausible energy manifold for the partition function, heat capacity variations for a cluster tissue glass have been evaluated which seems to simulate reasonably well the behaviour of real glasses. The glass transition in the model is controlled by the ground state vibrational frequency of the most mobile ion in the glass; for example, alkali ions in most alkali containing glasses. It could also be an anion such as halogens in lead oxyhalide glasses. If ΔE is the ground state vibrational energy of the mobile ion then,

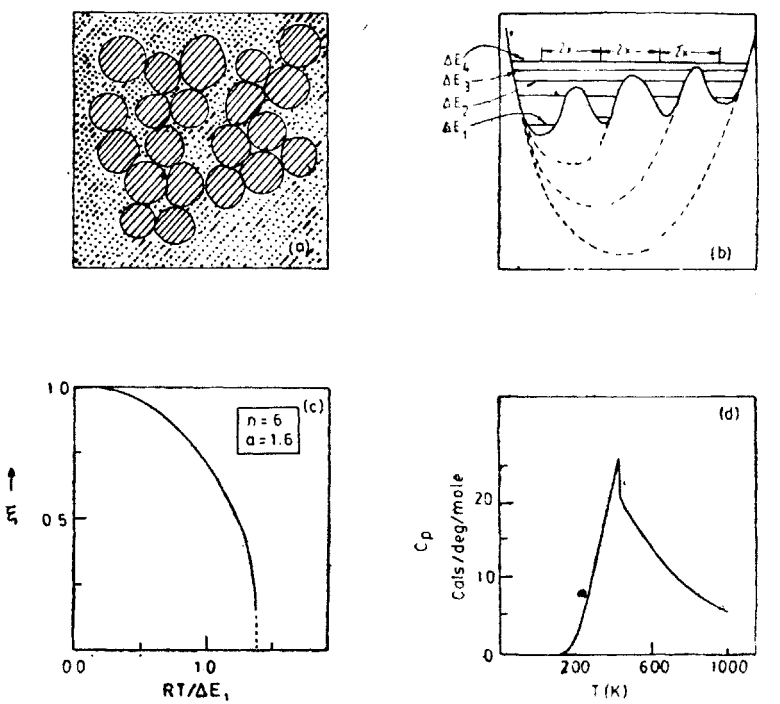


FIG 1 Cluster model of glasses.[10] (*a*) a schematic illustration of cluster-tissue texture, (*b*) a schematic of anhormonic potential wells which coalesce at higher energy levels. Energy differences ΔE_1, ΔE_2 etc. decrease and amplitudes (number of times $2x$) increase in higher vibrational levels, (*c*) variation of ξ with reduced temperature $RT/\Delta E$ (a is taken as 1.6 and number of vibrational states 6), (*d*) typical variation of configurational heat capacity in the model.

$$T_g = \frac{CR}{\Delta E},$$

where R is gas constant and C is a constant of the model whose value is between 1.2 and 1.6. It is interesting to note that T_g cannot exceed about 1110 K in view of the highest known cage vibrational frequencies. Ionic glasses have frozen entropies whose magnitudes are considerably low.[21] This is consistent with the cluster model. Since the clusters are highly ordered or microcrystalline, the glass can sustain only small magnitudes of configurational entropy in its tissue region which forms a minor component particularly in well-annealed glasses.

A further advantage of such a model is that the notion of soft mode[22] can be introduced in a natural manner to discuss the behaviour of glasses. As noted earlier, ions which populate systematically coalesced potential energy states with systematically increasing degree of coalescence possess systematically lower vibrational frequencies and their values ultimately approach zero towards T_g. Such are the soft modes germane to glass and their character is different from that of soft modes in crystals. Temperature behaviour of Lamb Mössbauer factors in glasses[23] can be understood on the basis of such soft modes.

Charged Defects and Covalent Glasses

Arsenic chalcogenides form typically covalently-bonded glasses. Particularly interesting are the series of glasses formed in As–Se system, all the way from Se to significantly As-rich ($As_{60}Se_{40}$) compositions. The structure of these glasses correspond to As–Se networks in which As is 3-coordinated and Se is 2-coordinated. A feature of structural interest in these glasses is that in compositions away from stoichiometric As_2Se_3, homoatomic bonding is to be expected as indeed the case. Since the energy of the heteroatom bond, As–Se, is significantly difierent and greater than energy of either of the homoatomic (As–As and Se–Se) bonds, maximum heteroatom bonds are first formed in the melt so that homoatomic As–As bonds are absent in Se-rich glasses and vice versa (Fig. 2)[24] a situation described as 'chemical ordering'[25] and is present in most chalcogenide glasses since heteroatom bond energies are higher than the pertinent homoatomic bond energies (by several times kT_m). Increase in electronegativity differences between the elements in glasses gives rise to increase in the ionic character of the bonds and hence, the heteroatomic bonding dominates. In fact, the ionic energy component due to heteroatom linkages can be so high that in oxide glasses, neither peroxy linkages nor the corresponding homoatomic counterpart (such as Si–Si, B–B etc linkages) coexist in the glasses formed from the high temperature melts due to their relative instability. Another feature of significance in covalent glasses is the constancy of local coordinations in their structures. By and large they remain fixed as for example $[SiO_{4/2}]$ tetrahedra, $[AsSe_{3/2}]$ pyramids, etc. The covalent network can be 1 or 2 or 3-dimensional as typified by S, As_2Se_3 and SiO_2. Glass properties, however, are isotropic due to the randomness in packing which eliminates the directionalities.

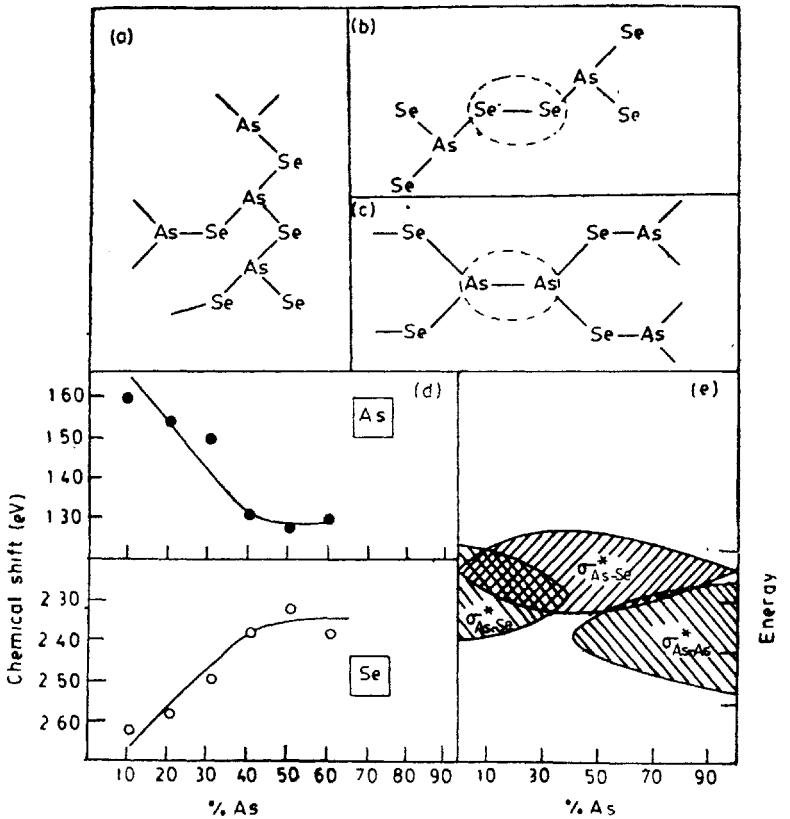
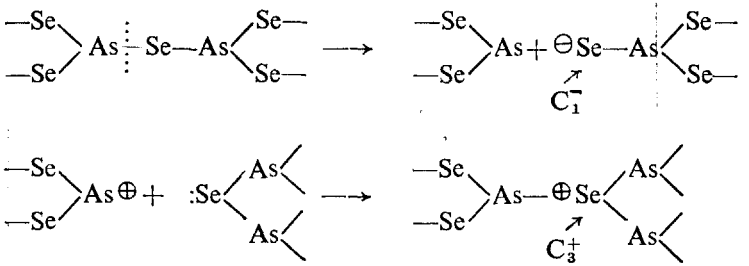


FIG 2 Chemical ordering in As–Se glasses. (*a*) structure of stoichiometric As_2Se_3 glass (*b*) structure Se-excess glass (*c*) structure of As-excess glass (*d*) variation of chemical shifts of As and Se in As–Se glasses as a function of composition, (*e*) a schematic of band energy diagram which is used to explain behaviour of chemical shifts.[21]

From a topological point of view, crystallinity of the covalent networks can in general be eliminated through introduction of either bond angle or bond length distributions. Comparison with model structures at least in fused quartz strongly support a spread in Si–O–Si bond angles.[26,27] In glasses of lower network dimensionality such as Se and As_2Se_3 inter network bonding is also significant. Indeed in As_2Se_3 the behaviour of glass-transition could be explained reasonably quantitatively by the excitation of inter layer secondary bonding.[28]

It is now known that all covalently bonded glasses are characterized by defects. The investigation of electron-transport in semiconducting chalcogenide glasses led to a more detailed formulation of these defects. Electron transport in chalcogenides was once thought to involve electrons present in 'dangling bonds' created by the homolytic scission of bonds. These localised electrons were supposed to populate levels in the gap.[29,30] Since electron spin resonance studies do not support the presence of unpaired spins consistent with the magnitude of conductivity, it was

postulated that dangling bonds redistribute electrons creating charged defects.[31,32] This in chemist's language is the heterolytic bond breaking. Chalcogenides carrying lone pairs of electrons readily coordinate to the positive species created in bond breaking thereby restoring the loss of covalent bond as shown below :



The net effect is the creation of a defect pair, C_3^+ and C_1^- (where C is the chalcogenide), the over- and under-coordinated chalcogenides respectively at a net expense of energy required for pairing electrons in the valence orbital of the chalcogen. Such pairs of defects as known as conjugate pairs of defects[33,34] which we believe play a dominant role in covalent chalcogenides glasses. Consider, for example transport could occur through the reverse process in which defects are annihilated and recreated by the reaction

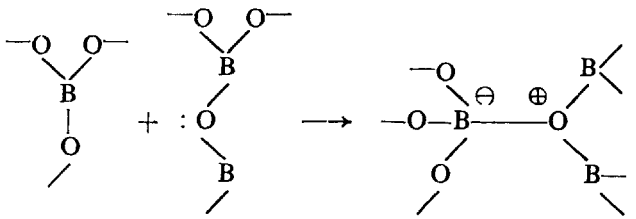
$$C_3^+ + C_1^- \rightarrow 2C_2^0 \rightarrow C_1^- + C_3^+$$

The reaction occurs with neutral state as activation stage; the recreated pairs could be present at a point further down in the direction of the field and the process amounts to transfer of a charged centre or two electrons (or equivalently two holes). The activation barrier would, therefore, correspond to the energy required for the creation of defect pairs. Indeed, the experimental d.c. conductivity activation energies have been shown to be equal to the energy required for creation of conjugate pairs of defects in a large number of amorphous chalcogenides.[33] The conductivity is due to thermally assisted hopping of charged defects which are bipolarons. This aspect has been confirmed through linearity of log $\sigma T^{-2/5}$ plots.[35]

The primary feature of charged defect model is that it conserves the total number of covalent bonds at the expense of a relatively lower energy required for electron pairing. What is not usually as well appreciated is that charged pair creation brings two more bonus advantages for the glassy state. Firstly, it allows for snapping of a covalent bond where an incovenient degree of bonding strain develops during the growth of amorphous structure. This is crucial in ridding ordered arrangement of atoms. Secondly and more importantly, it introduces charged centres which provide for additional ionic interactions while conserving the total number of covalent linkages. This stabilies energetically the glass network. Such defects, therefore, may be a common feature of all glasses which contain lone pair bearing elements like oxygen and chalcogens. In silica glass, for example, formation of conjugate pairs charged defects like $[O\text{-}Si_{3/4}]^+$ and $[O\text{-}Si_{1/4}]^-$ centres

may help terminate the strains created by cumulative distortion effects upon basic quartz structure. A model of SiO_2 glass would, therefore, suggest presence of clusters of essentially quartz-like structure mediated by thin walls of tissue consisting of a large density of conjugate defect pairs of over- and under-coordinated oxygen. It is worth examining whether such defect pairs are responsible for some of the anamolous properties of fused quartz.[36]

It is well known that B_2O_3 can be crystallized only with difficulty[37] and melts of B_2O_3 exhibit properties consistent with fluids with three-dimensional networks[38] rather than with two-dimensional networks. It would be tempting to attribute these features to the additional bonding made possible through charge defects of the following type :—



Formation of tetrahedral boron though participation of the lone pair on oxygen should be exothermic combining both covalent and coulombic interactions. Presence of such stable defects therefore may generate a structural resistence to nucleation of the crystalline B_2O_3 melts. It would also account for the three-dimensional network character of B_2O_3 melts. We shall see a little later that charged defect pairs which interact through coulombic forces play a significant role in molybdophosphate glasses also.

Glasses with Octahedral Motifs

It has been the general belief that in glasses coordination numbers are low (2 to 4) in conformity with Zacharisen's model. We have already noted that in ionic glasses which are dominated by non-directional bonding, the participating ions tend to acquire maximum coordination subject only to geometrical constraints. Therefore, an ionic glass, constitutes an antithesis of Zacharisen's glasses. Even in cases where covalency of bonding dominates, as in the novel glass systems like molydophosphate and lead oxyhalides octahedrally coordinated structural units form the primary motifs. In fast-ion conducting AgI–Ag_2O–MoO_3 glasses molybdenum is present in discrete MoO_4^{2-} tetrahedral ions. But in this glass system, the oxygen ion activity is high and stabilizes the tetrahedral MoO_4^{2-}.[7,39] In molybdophosphates, however, due to high formal valence states of phosphorous and molybdenum, metal-oxygen linkages are largely covalent. In the absence of oxygen ion activity Mo is present in formally netural $[MoO_{6/2}]$ units in which hybridized d^2sp^3-orbitals of Mo are used for bonding with oxygen. Equilimolar MoO_3–P_2O_5 glass corresponds to chemically ordered network of $[MoO_{6/2}]$ and $[PO_{3/2}]$ units with all but two

corner shared oxygen.[40] One of the oxygens io $[POO_{3/2}]$ units are attached to the phosphorus atom through a double bond. Mo-O bond is as covalent as Si-O bond and the structure is therefore adequately described as a three-dimensional covalent network. The effect of modifiers may be discussed in the same manner as in silicate glasses. Modification with alkali oxides which release O^{2-} ions for bond-breaking increases the oxygen ion activity and when more than two -Mo-O-Mo- or -Mo-O-P- linkages are broken, resulting $[MoC_{4/2}O_2]^{2-}$ units convert themselves into $[MoO_4]^{2-}$ units. Conversion is easy because $[MoO_4^{2-}$ units have roughly the same rotational volume as occupied by $[MoO_{6/2}]$ units. Conversion of $[MoO_{4/2}O_2]^{2-}$ units are both evidenced in IR spectra and inferred in several properties of glasses.[40]

Mo^{6+} is often reduced with facility to Mo^{5+} at the higher temperature employed for the glass preparation. This reduction leads to loss of oxygen. The glasses formed are quite stable, coloured and give rise to characteristic ESR spectra. Here also charged defect pairs, but of a slightly different nature appear to play an important role.[40] While the octahedron around Mo^{5+} is negatively charged, the structure of octahedron is retained without the loss of a corner by the ready participation of an otherwise unshared oxygen attached to phosphorus through a double bond. The process may be represented as follows :—

$$2[Mo^{IV}O_{6/2}] \rightleftharpoons 2[Mo^{VI}O_{5/2}\square]^{+} + O^{2-}$$

$$O^{2-} \rightleftharpoons \tfrac{1}{2}O_2 + 2e$$

$$2[Mo^{VI}O_{5/2}\square]^{+} + 2e \rightleftharpoons 2[Mo^{V}O_{5/2}\square]$$

$$2[Mo^{V}O_{5/2}\square] + 2[POO_{3/2}] \rightleftharpoons 2[Mo^{V}O_{6/2}]^{-} + 2[PO_{4/2}]^{+}$$

In the process, $[POO_{3/2}]$ unit is converted into $[PO_{4/2}]^{+}$ unit and is paired to $[MoO_{6/2}]^{-}$ unit. By the creation of such paired defects, structural features are retained, coulombing energy term is added and further cross-linking is achieved through 4-connected phosphate units.

The apparently facile nature of the conversion of $[POO_{3/2}]$ unit into a charge bearing $[PO_{4/2}]^{+}$ is exploited by additives like PbO which possess a tendency to occupy covalently bonded tetrahedral network positions.[41,42] In order to incorporate lead as $[PbO_{4/2}]^{2-}$ units in to the network, $[POO_{3/2}]$ units readily share the unshared corner resulting in $[PbO_{4/2}[^{2-} : 2[PO_{4/2}]^{+}$ complexes. Once the $[POO_{3/2}]$ to $[PO_{4/2}]^{+}$ conversion is exhausted for want of $[POO_{3/2}]$ units, further addition of PbO begins to play the role of a modifier oxide like K_2O. Thus, in the presence of modifier PbO Mo^{5+} has little tendency to stabilize and the concentration of Mo^{5+} becomes low. These features are confirmed from ESR[41] and ultrasonic[43] investigations (Fig. 3). In all their structural and important physical properties, phoshotungstate glasses are very similar to phospho-molybdate glasses.[41]

Lead Oxyhalide Glasses

Lead oxyhalides are again among novel glass systems[43,47] where the structure is built of $[PbO_2X_4]$ (X = F, Cl) octahedral units.[48] The components of these glasses

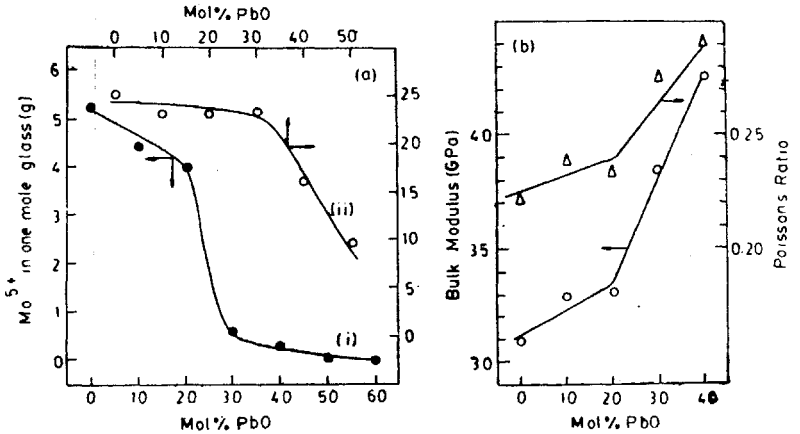


FIG 3 Mo^{5+} concentrations in lead phosphomolybdate glasses. (*a*) variation of Mo in (*i*) (80-*x*) MoO_3-*x* PbO-20P_2O_5 glasses (*ii*) in (60-*x*) MoO_3-*x*PbO-40Pb_2O_5 glasses, sharp drop occurs in Mo^{5+} concentration as soon as concentration of PbO and P_2O_5 become equal, (*b*) variation of bulk modulus and Poisson's ratio in (80-*x*) MoO_3-*x* PbO-20P_2O_5 glasses Here again trends in variation of elastic properties change when PbO concentration becomes equal to the concentration of P_2O_5 (*see* text).

namely PbO and PbX_2 (PbF_2 or $PbCl_2$) are known to be typical examples of covalently and ionically bonded solids respectively.[49] While PbO and PbX_2 are themselves not good glass-formers, glasses containing 40–90 per cent PbO may be conveniently prepared. The halide rich glass compositions are characterized by high degree of ionicity. Presence of [PbO_2X_4] octahedral motif in all glasses was first postulated to account for the pair distribution functions obtained from X-ray diffraction measurements and were subsequently confirmed from detailed EXAFS investigation of the glasses.[46,50]

Linkages of the type –O–Pb–O– form networks whose dimensionality and extent are reduced in halide-rich glasses in which O/Pb ratio decreases considerably. It is interesting to note that glass formation ceases in compositions where the linkages do not extend beyond –Pb–O–Pb–. The bond angle OPbO which is close to 90° in oxide-rich glasses as a consequence of *p*-orbital bonding of Pb to oxygen atoms gradually opens up as the ionicity increases in halide-rich glasses and the overall symmetry of [PbO_2X_4] units evolve from $C_s \rightarrow C_{2v} \rightarrow D_{4h}$ as the halide concentration in the glass increases. These features have been confirmed from an analysis of X-ray absorption near edge structures (XANES) associated with Pb–L-edges (L_1, L_2 and L_3) in glasses (Fig. 4).[51] The nature of bonding in [PbO_2X_4] units can be understood in terms of suitable molecular orbital diagrams which involve the 6*d*-orbitals of Pb.

The nature of bonding in PbO–PbX_2 glasses is affected by the application of pressure on the glass.[44] In fact, crystallization occurs under pressure in both PbO–$PbCl_2$ and PbO–PbF_2 glasses in which Pb–O bond appears to get modified

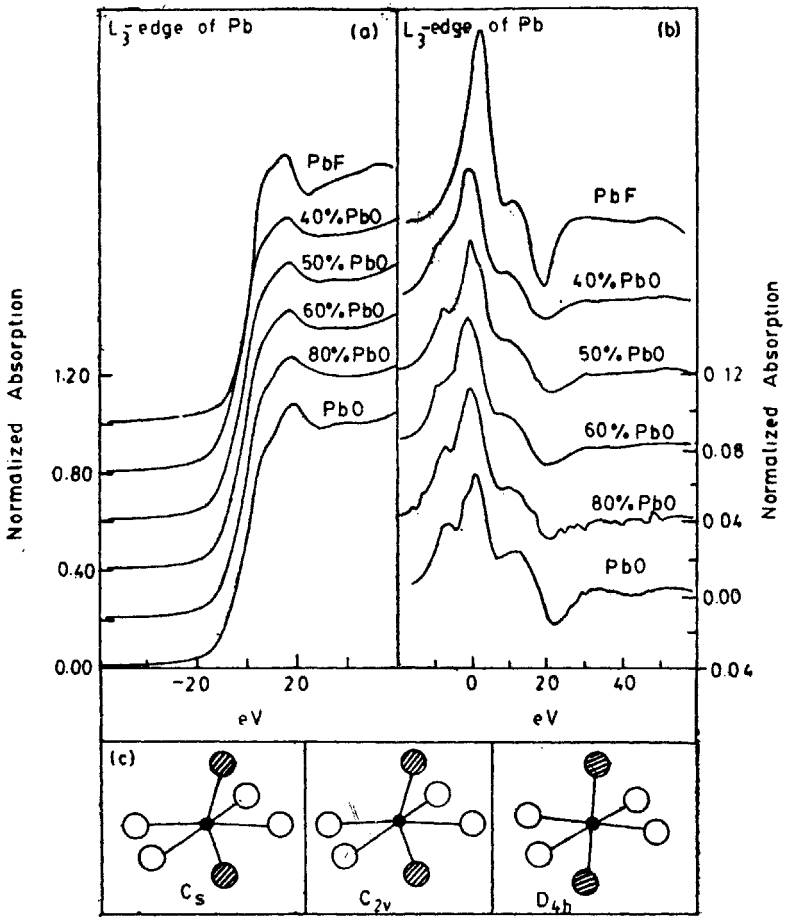


FIG 4 Bonding and structure of $[PbO_2F_4]$ units in $PbO–PbF_2$ glasses : (*a*) X-ray absorption near edge structure (XANES) of $PbO–PbF_2$ glasses along with those of PbF_2, (*b*) differentiated spectra corresponding to those in (*a*) in which absorption peaks are more clearly defined. (*c*) The structural units whose MO diagrams were found account for the features in the spectra.

leading to formation of O^{2-} ions. In oxychloride glasses in particular rearrangement into a crystalline product is assisted by formation of O^{2-} ions.

Hence, the structural aspects of molybdo phosphates and lead oxyhalide glasses provide evidence for the prevalence of octahedral motifs in and compatibility with the glassy state. Octahedral geometries seem to occur wherever *d*-orbital participation becomes energetically feasible.

COVALENCY AND GLASSY STATE

One of the traditional beliefs in glass science has been that good glass formers are highly covalently bonded.[52] The attributes of covalent-bonding are directionality

of bonding and shortness of the range of interaction (ideally confined to the connected pair). Both these features are considered to be factors contributing to facile elimination of long-range order necessary for glass formation. However, fully covalently bonded elements like silicon and carbon do not form glasses. It appears to us that the flatness of the -M-O- or -M-C-M- bond flexing potential is responsible in a major way for easy glass formation. Oxygen and chalcogens possess certain unique properties which may contribute to the glass-forming tendency; reasonably high electronegativity, and presence of lone pairs which can be engaged in additional bonding in extreme situations etc. It is also apparent that sixth group elements are unique in and dominate the glass chemistry.

Nevertheless, M-O bonds in glasses in general appear to become more covalent in glassy state than they are in the corresponding crystalline state.[53,54] This feature was first observed through chemical shifts in X-ray absorption edges.[55] The increase in covalency manifests quite generally as increase of edge absorption coefficients.[45,51,56,57] The absorption edges correspond to excitations from core levels of the atoms to allowed vacant final states (atomic, molecular or band-like). The bonding details affect the transition dipole matrix element and thereby the absorption coefficient which is related to the square of the matrix element. Since increase in covalency may be considered as corresponding to reverse transfer of bonding electrons from the anion, these electrons affect the final states through enhanced shielding. Thus, intensity variations are quantitatively correlated to number of covalent electrons through shielding constants.[57] The extent of covalency itself may thus be quantified. In fact, it can be shown that the absorption coefficient μ_{cov}, of the covalently bonded atom and absorption coefficient μ_{ion} of the same in free ionic state are related as $\mu_{cov} = \mu_{ion} \exp [aS]$; where S is the shielding due to covalent electrons (involved in covalency) and a is a constant determined by connected quantum states in the free ion.

Investigation of L-edge spectra of Nd in NdF_3-BeF_2 glasses,[56] of Th in ThF_4-HfH_4 glasses[45] and of Pb in PbO-PbX_2 glasses[51] have revealed that the bonding is always more covalent in glasses than in crystalline state. This is intriguing because increasing covalency generally leads to loss of total cohesive energy. But considering that glass has a lower density than the corresponding crystalline phase, loss of coulombic interactions is likely to be made up by a local enhancement of covalency.

Physical Models of Glasses and their Limitations

The two general physical models employed in the description of glasses are the random network model and the random close packing model. Random network model is generally considered adequate for describing covalent glasses such as fused quartz. Distribution in Si-O-Si bond angles eliminates periodicity in glassy SiO_2. The absence of such angle distributions induce an order characteristic of crystalline modifications like β-quartz. The distribution of bond angles is now well established through solid state high resolution magic-angle-spinning NMR

which has also been used to investigate structural species in modified silicate glasses.[46a]

Random close packing on the other hand has been found to be particularly useful to model the structure of metallic glasses. Indeed, a close correspondence exists between random close packing and random network in that the interconnection of the tetrahedral voids of the rcp model generates a three-dimensional random network of tetrahedra.

From all the previous discussions it is obvious that ionic glasses cannot be described by either of these physical models without unduly severe modification. One could of course introduce artefacts of network decoration and attempt to use random network model to describe networks containing octahedra but once again it would underscore the necessity for more satisfactory structural models.

One serious question that such physical models do not address themselves to is, 'what is the origin of bond angle distribution itself?' The apparent reluctance of simple glasses such as fused quartz and B_2O_3 to crystallize even when a high degree of thermal energy is available suggests that the amorphous state with its frozen bond angle distribution is perhaps energetically not unfavourable. Whether there exists an inherent tendency to generate bond angle or bond length distributions does not form the subject matter of the physical models.

Acid-Base Concept and Chemical Model of Glasses

It is common chemical knowledge that all heteroatom bonds are characterized by mixed type of bonding, in particular ionic-covalent type in inorganic materials.[59–61] direction of the transfer of electron is from a cation to an anion or from a Lewis The acid to a Lewis base. Such bonding electron displacements are due to electronegativity differences. The acid-base concept is therefore rooted in the concept of electronegativity. The acid-base formalism is empirical and has been developed quite successfully. Parameterized values for acidity and basicity have been tabulated and a number chemical phenomena have been rationalized using such parameters.

One empirical measure of acidity of a cation is its bond valence corrected for the variation of the bond distance.[62] The acidity or partial valence, s, and bond distance R are related as

$$s = \left(\frac{R}{R_0}\right)^{-N},$$

where R_0 and N are constants derived from analysis of crystal structure data from literally hundreds of compounds with a variety of coordination numbers. A large difference in the acidity of the cation and the basicity of the coordinating anion in a compound is an indication of the latter's reactivity or instability. Such a compound generally exhibits a tendency to acquire into its structure other atoms or groups of

atoms which ameliorate the imbalance in acid-base parameters. The imbalance can also be atoned by local distortions which alter the bond lengths in accordance with the above relation and increase or decrease the value of s. Thus a distortion would be introduced into the structure in order to atone differences in acid-base parameters wherever large differences exist. Such distortions would therefore reflect natural difficulty in crystalline packing or tendency for glass formation. Acid-base parameters of a few good glass-formers are presented in Table I below and it may be noted that the cation acidities are indeed quite different and much larger than the anion basicities :

TABLE I

Acid-base parameters of good glass formers

	acidity (a)	*basicity* (b)	(a/b)
SiO_2	0.95	0.50	1.9
B_2O_3	0.88	0.50	1.8
P_2O_5	1.30	0.50	2.6
TeO_2	1.06	0.50	2.12
$ZnCl_2$	0.36	0.10	3.6
BeF_2	0.50	0.21	2.4

One would, therefore, expect oxygen or other anions to displace themselves in such a way that the resulting bond distortions would increase their net valences. The acid-base model thus provides a reasonable explanation of inherent glass-forming tendency in some materials. It would, therefore, be worthwhile examining this aspect further.

It would be equally profitable to ponder on the variations in electronegativities due to changes in hybridization of anions particularly oxygen. The different levels of s-mixing in the bonding orbitals of oxygen would not only introduce a distribution of bond angles but a distribution of bond electronegativities of oxygen atoms. The equilibrium cation-oxygen distances (the corresponding bond strengths) (due to different ionicities) would, therefore, again acquire a distribution in accordence with the principle of electronegativity equalization in the formation of chemical bonds. This would also contribute to an inherent glass-forming tendency because of the resulting basic symmetry in local configurations.

CONCLUSION

An attempt has been made in this presentation to show that structure stability and several properties of glasses are intimately connected to the nature of chemical bonds in them. Physical theories in their search for unifying models tend to underestimate, if not ignore, the bonding aspects. Models based on chemical approaches with their strong empirical base may therefore be expected to provide new and profitable insights.

Acknowledgements

I should like to thank Professor C N R Rao for many educative discussions related to physical chemistry of glasses spread over years and for his kind encouragement. Thanks are due to Mr U Selvaraj who helped me in preparing the manuscript.

References

1. H Rawson *Inorganic Glass-Forming Systems* Academic Press London (1967)
2. R H Doremus *Glass Science* Wiley New York (1973)
3. A E Owen *Contemp Phys* **11** (1970) 227 257
4. P S L Narasimham and K J Rao *J non-cryst Solids* **27** (1978) 225
5. P S L Narasimham and K J Rao *Proc Indian Acad Sci* **A87** (1978) 275
6. H G K Sundar and K J Rao *J chem Soc Faraday* I **76** (1980) 1617
7. S Hemlata and K J Rao *J non-cryst Solids* **54** (1983) 313

7*a*. K J Rao *Preparation and Characterization of Materials* (*Ed* J M Honig and C N R Rao) Academic Press New York

8. K J Rao and C N R Rao *Mater Res Bull* **17** (1982) 1337
9. R Parthasarathy K J Rao and C N R Rao *Chem Soc Rev* **12** (1983) 361
10. K J Rao *Proc Indian Acad Sci* **93** (1984) 389
11. S Hemlata G Parshasarathy S T Laxmi Kumar and K J Rao *Phil Mag* **47** (1983) 29
12. S Hemlata G Parthasarathy K J Rao and E S R Gopal *Pramana* **27** (1984) L269
13. L Bursill K J Rao and J M Thomas *Nature* **289** (1980) 157
14. P H Gaskell D J Smith C J D Catto and J R A Cleaver *Nature* **281** (1979) 465
15. R Parthasarathy K J Rao and C N R Rao *J phys Chem* **85** (1981) 3085
16. H G K Sundar R Parthasarathy and K J Rao *Z Naturforsch* **A37** (1982) 191
17. J C Phillips *J non-cryst Solids* 44 (1981) 17; *Solid State Phys* **37** (1982) 93
18. S Sakka and J D Mackenzie *J non-cryst Solids* **6** (1971) 145
19. K J Rao *Bull Mater Sci* **1** (1979) 181
20. C N R Rao and K J Rao *Phase Transitions in Solids* McGraw-Hill London (1979)
21. C A Angell and W Sichina *Ann N Y Acad Sci* **279** (1976) 53
22. P A Flinn B J Zabransky and S L Ruby *J Phys C* 6 **37** (1976) 745
23. Seetha Bharathi R Parthasarathy K J Rao and C N R Rao *Solid State Commun* **46** (1983) 457
24. K J Rao R Mohan P R Sarode and M S Hegde *Pramana* **16** (1981) 309
25. G Lucovsky *Phys Rev* **B15** (1977) 5762
26. R L Mozzi and B E Warren *J appl Cryst* **2** (1969) 164
27. R J Bell and P Dean *Phil Mag* **25** (1972) 1381
28. K J Rao and R Mohan *J phys Chem* **84** (1980) 1917
29. N F Mott and E A Davis *Electronic Processes in Non-Crystalline Materials* Clarendon Press Oxford (1979)
30. S R Elliott *Physics of Non-Crystalline Materials* Longman London (1984)
31. N F Mott E A Davis and R A Street *Phil Mag* **32** (1975) 961
32. M Kastner D Adler and H Fritzsche *Phys Rev Lett* **37** (1976) 1504
33. K J Rao and R Mohan *Solid State Commun* **39** (1981) 1065
34. R Mohan and K J Rao *Indian J Chem* **20A** (1981) 864
35. R Mohan and K J Rao *Mater Res Bull* **18** (1983) 195
36. O L Anderson and H F Bommel *J Am ceram Soc* **38** (1955) 125
37. M J Aziz N Nygren and D Turnbull *J appl Phys* **57** (1985) 2233

38. B Bridge N D Patel and D N Waters *Phys Stat Sol* **77** (1983) 655
39. K J Rao and J Wong and S Hemlata *Proc Indian Acad Sci* **94** (1985*c*) 449
40. U Selvaraj and K J Rao *J non-cryst Solids* **72** (1985) 315
41. U Selvaraj and K J Rao (1986) (*to be published*)
42. K V Damodaran U Selvaraj and K J Rao (1986) (*to be published*)
43. B G Rao H G K Sunder and K J Rao *J chem Soc Faraday I* **80** (1984) 3491
44. K J Rao G Parthasarathy B G Rao and E S R Gopal *Mater Res Bull* **19** (1984) 1221
45. K J Rao J Wong and M W Shafer *J Solid State Chem* **55** (1984) 110
46. K J Rao J Wong and B G Rao *Phys Chem Glasses* **25** (1984) 57;
42*a*. C N R Rao J M Thomas J Klinowshig V Selvaraj K J Rao J R Millivard and S Ramdas *Angew Chem* **24** (1985) 61
47. K J Rao S R Elliott and B G Rao *J Mater Sci* **20** (1985) 1678
48. B G Rao and K J Rao *Phys Chem Glasses* **57** (1984) 11
49. A F Wells *Structural Inorganic Chemistry* Oxford University Press Oxford (1975)
50. B G Rao K J Rao and J Wong (1986) (*to be published*)
51. K J Rao B G Rao and J Wong *J chem Phys* (1986) (*to be appear*)
52. L D Pye H J Stevens and W C La Course *Introduction to Glass Science* Plenum Press New York (1972)
53. V P Prjanishnikov G M Bartever A D Zignov and V V Gorbachev *Proc 9th int Congr Glass* (1971)
54. G G Long A G Reversz and M Kuriyama *J non-cryst Solids* **70** (1985) 271
55. C N R Rao R Parthasarathy P R Sarode and K J Rao *Phil Mag* **41** (1980) 582
56. K J Rao J Wong and M J Weber *J chem Phys* **78** (1983) 6228
57. K J Rao *J Indian Chem Soc* **63** (1986) 87
58. U Selvaraj K J Rao C N R Rao J Klinowsky and J M Thomas *Chem Phys Lett* **114** (1985) 24
59. L Pauling *Nature of the Chemical Bond* Cornell University Press Ithaca (1960)
60. J E Huheey *Inorganic Chemistry* Harper International New York (1978)
61. R T Sanderson *Chemical Bonds and Bond Energy* Academic Press New York (1976)
62. I Brown In : *Structure and Bonding in Crystals* (*Ed* M O'Keeffe and A Navortsky) Academic Press New York (1981)