[Both academic and technological interests have caused a great revival of research in glass science. The twin freedoms enjoyed by materials in glassy state, namely, freedom from restraints of periodicity and freedom from requirements of stoichiometry, make the study of glasses an area of great research interest. The rate of growth of research during the last decade has also been phenomenal. 'Current trends in glass research' by Dr. Rao gives a bird's eye view of the prominent trends of research in glass.—Ed.]

CURRENT TRENDS IN GLASS RESEARCH

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IN a Festschrift volume brought out on the occasion of the award of Nobel prize to Professor N. F. Mott, one of the authors[1] wrote, 'for having "done so much to transfer glass science from the archieves to the forefront of solid state"' Indeed, these words of dedication serve as a summary pointer to the flurry of activities in the area of glass science today. The challenges of the glassy state are multifaceted. Many new glass forming systems are being discovered and reported; and there have arisen a variety of new problems which require alterations or extensions of the existing theoretical framework in order to provide answers to them.

In such an expanding and expansive frontier of physical science, to characterize some areas of research as 'trends' cannot be expected to be uniquely satisfactory; but in this article, effort is directed to highlight some important areas of current interest and the impact of such research work, in understanding the glassy state.

Experimental Techniques

Almost every physical technique has been used in the investigation of glasses. Notable among those which have provided crucial information in understanding the glassy state, in recent times are the small angle X-ray scattering (SAXS), neutron scattering, nuclear magnetic resonance NMR, high resolution electron microscopy and extended X-ray absorption fine structure (EXAFS) analysis. Application of SAXS and neutron scattering to analysis of glass structures has been reviewed by Wright and Leadbetter[2]. Much has been understood about borate glasses by the use of ^{10}B and ^{11}B NMR through the monumental contributions of Bray and co-workers[3]. It is now known that the building blocks in borate glasses consist of the five different types of boron-oxygen groupings predicted much earlier by Krogh-Moe[4]. Similarly the use of appropriate magnetic nuclei should be of great value in understanding structures of many other glasses. High resolution electron microscopy combined with the techniques of image synthesis (using computers) has provided, perhaps, the most spectacular information on glasses. The existence of ordered regions with crystalline motifs can be recognised through the appearance of fringes. Gaskell *et al.*[5] and Bursill *et al.*[6] have shown that such ordered regions do exist in a variety of glasses. These observations will prove very crucial in developing a viable model for glasses.

EXAFS analysis is definitely the most significant development in recent times[7]. Since the absorption edge energies are atom specific, EXAFS can provide pair correlation information with respect to the particular type of atoms. The technique is quite sensitive and EXAFS data have revealed[8] the presence of short Se–Se distances in selenium glass, corresponding to the presence of π-bonded selenium chain terminations which could also act as charged defect centres. However, the technique is known to be less

sensitive to structural details beyond the first shell of atoms, and therefore, is a powerful tool primarily for the understanding of local configurations. The theory of EXAFS seems to be well understood, though certain features like focussing effect[9], etc., are not.

Glass Systems of Current Interest

Several glass forming systems are attracting considerable attention in recent times and some of them on account of the needs of industry. Oxygen free glasses, particularly those based on beryllium fluoride[10,11], have potential applications in areas requiring extended UV transmission and also in lasers (since these glasses are known to have very low refractive indices). Glass systems consisting of heavy metal fluorides such as ZrF_4, BaF_2 and ThF_4 are likely to prove good fast ion (anion) conducting glasses[12]. Jack[13] has reported nitrogen containing 'sialon' glasses. Many substituted sialon glasses have also been reported recently[14,15]. Since these oxy-nitride glasses are good self-nucleating systems, they can give rise to extremely valuable high temperature ceramics. It is now established that one out of every seven oxygen atoms, in aluminium silicate glasses can be replaced by nitrogen. A large variety of metallic glasses are being investigated[16], since met-glasses can be employed as materials of very useful mechanical and magnetic properties. Glasses required for optical communication are primarily based on silica and germania, though B_2O_3 and P_2O_5 are also often used in combination. Various aspects of optical quality glass fibres for application in optical communication have been reported recently[17,18]

Another important class of glasses is the chalcogenides as they have important applications[19] in the field of infrared transmission, xerography, optical mass memory and fast electronic switching. One of the chalcogenide glass forming systems reported recently[20] relates to Ge–Bi–Se–Te glasses in which it has been observed that *n*-type semiconductors are formed when more than 10 atom per cent of Bi is present. However, all the known chalcogenide glasses are only *p*-type semiconductors.

Several ionic glasses consisting of discrete anions such as AgI-Ag_2MoO_4, etc., are attracting attention because they are found[21] to be very good fast ion conductors. Many other glass systems[22] with condensed anions such as the silicates and borates containing Li^+ ions have also been found to be potential fast ion conductors in glassy state.

Fast Ion Conduction in Glasses

Very low activation energies (0·2–0·6 eV) for ion transport and consequently significantly large values of conductivity, σ (of the order of 10^{-2} to 10^{-7} ohm^{-1} cm^{-1}) are characteristics of fast ion conducting glasses. The conducting species in several glasses happen to be either Ag^+ or Li^+ ions. As mentioned earlier, fluoride systems such as ZrF_4–BiF_2–ThF_4 with F^- (anion) conducting species have also been reported. Various AgI based FICs have been investigated by Minami and coworkers[21, 23] and recent progress has been excellently reviewed by Tuller, Button and Uhlmann[22]. It is interesting to note that AgI, which is itself a fast ion conductor in high temperature crystalline form, is a major component of glassy Ag–FICs. Values of σ_0 (high temperature limiting conductivity) of glassy FICs are generally low, which means that the corresponding attempt frequency or the vibrational frequency of (charge transporting) ion is low. It implies a limitation of the notion of ionic hopping. There is the possibility of field assisted concerted drift of the Ag^+ ions in glassy FICs. If there are ordered regions, even approximatively of the size of 100 Å, and with compositions corresponding to substituted AgI, it should be easy to visualise the origin of the observed similarities of fast ion conduction in crystalline and glassy states[24]. The relevance of crystal chemical considerations in discussing problems of glassy state also becomes quite apparent.

Mixed Ion Effect

Mixed alkali effect is a phenomenon where anomalous variations in properties of glasses

occur when two alkali ions are present. Occurrence of mixed alkali effect has been found to be a feature of even ionic glasses[25] It is now appropriate to call it mixed ion effect, since the presence of two isovalent anions in glasses also, seems to produce anomalous variation in their properties[26]. Various theoretical approaches have been made to explain the origin of mixed alkali effect and the subject has been reviewed by Isard[27] and Day[28]. Mixed ion effect is basically a concomitant of ionic environment and it would, therefore, be appropriate to emphasise the influence of local geometries around the cations. Indeed, it has been found[25] advantageous to invoke the presence of local strain fields which affect the mobilities of cations in accounting for the mixed alkali effect in sulphate glasses. The presence and influence of such micro strain fields cannot be ruled out even in network forming glasses in which the atoms surrounding the cations are essentially ionically bonded[24]. Cage-like characteristic vibrational modes of alkali ions have been reported to be present in mixed alkali glasses[29,30] These frequencies do not seem to be affected by inter-alkali concentration variation[30]. Therefore, it suggests that electrodynamic interactions[31], if any, may not play a vital role in mixed alkali effect. The advantage of emphasising packing and strain aspects becomes more apparent when the presence of similar anomalies is noted in mixed anion glasses. However, mixed ion effects remain at present a subject of considerable interest and curiosity.

Modelling, Computer Simulation and Structure of Glasses

Our understanding of the structure of glasses today remains at best ambiguous. While description of glasses as disordered solids convey a qualitative understanding of the nature of glasses, a quantification of the disorder[32] has not been possible at all. The scattering experiments at best provide a radial distribution function (RDF) which only constitutes an average representation of the structure[33]. Meaningful interpretation of such RDFs invariably require the assistance of laboratory or computer built models. Two important types of such models have been the random network model[34, 35] and the random close packing model[36, 37] Random network model which is most favoured for fused silica, and such other covalently bonded materials is based on the fact that three-dimensional periodicity of a connected lattice can be eliminated by introduction of small distribution of bond angles and/or bond distances. Random close packing model which is based on the classic work of Bernel[36, 38] uses the concept of close packing of phserical objects of identical or varying sizes in space without inducing ordering in any manner. But as pointed out earlier, high resolution electron microscopy[5,6] of glasses suggest that sufficiently high correlations exist over short distances. Studies in metallic glasses[16] also seem to suggest strong correlations over short distances of 10–15 Å. Understanding of glassy state has also been assisted substantially by computer simulation. Two well-known simulation procedures have been the so-called Monte-Carlo (MC) and molecular dynamics (MD) calculations. Both approaches (though involve unphysically large cooling rates) have indicated that on cooling a system from molten state vitrification results at a temperature which can be recognized as glass transition temperature, T_g. The influence of the various interaction potentials on the characteristics of glass transition in computer experiments has been reviewed by Angell *et al.*[39]. A significant observation in computer experiments is the formation of clusters in the molten state prior to the glass transition. Various aspects related to such cluster formation have been reviewed by Hoare[40] and Hoare and Baker[41].

Considered together the results of computer experiments and high resolution electron microscopy suggest the formation of clusters (prior to the glass transition) as a melt is subjected to cooling. These clusters may have both crystalline and non-crystalline motifs Indeed laboratory built models of tetrahedral glasses also suggested[42] existence of ordered regions in spite of all care exercised during model building. It is, therefore, now clear

that there cannot be any unified structural model for all glasses. The existence of short range order is perhaps inescapable and its details are likely to be dictated by the requirement of optimally low free energy of the clusters. Inherent to such disordered solids should be the presence of a configurational entropy[43]. It is often measured in real systems as the excess or frozen entropy. However, it would be interesting to visualise a disordered solid with the structural prescriptions summarized above and possessing vanishing configurational entropy. Such has been the description of the so-called ideal glass[44].

Glass Transition Phenomenon

A unique feature which distinguishes glasses from the rest of the amorphous materials is the occurrence of glass transition[45]. An understanding of this has eluded many efforts to date. While the free volume theory[46] is both elegant and conceptually simple, it has inherent weaknesses in the context of pressure effects[47] on the glass transition. Entropy approach, the development of which is largely due to Gibbs and co-workers[48] has been by far the most successful in accounting for several features of an experimental glass transition. But these approaches are based on the assumption that a theory for thermal variation of a suitably chosen property of liquids in the supercooled region should naturally account for all aspects of glass transition. The kinetic features of the non-equilibrium, high viscosity regime of a supercooled (metastable) liquid, prior to the glass transition, renders the situation extremely complex. Evaluation of any thermodynamic theory becomes unfeasible. Features like variation of transport properties as $\exp[\pm E_a/(T - T_0)]$ (where E_a is an activation barrier and T_0 a constant with units of temperature) are also not sufficiently universal[49,50], to be relied upon, as basis for developing new theoretical approaches[51].

In this context the relatively recent experimental observation on cluster formation assumes considerable importance. The suggestion that congealation of clusters leads to glass transition, a view that was expressed by Tammann[52] long ago (though provokingly discussed by Hoare[40]) perhaps represents a more promising model of glass transition. Formation of clusters in supercooled liquids prior to glass transition has been evidenced in ESR spectroscopic studies of organic glasses[53]. It still remains to be understood as to what factors influence cluster formation and, how to formulate the problem of cluster congealation.

If the clusters happen to have crystalline motifs, effect of slow cooling can be looked upon as assisting the growth of these clusters at the expense of the inter-cluster material. Then, it would lead to a very interesting possibility[24]. An ideal glass corresponding to one obtained at an infinitely slow cooling rate would correspond to an aggregate of such (crystalline) clusters. Further, such glasses would have no inter-cluster material and therefore no configurational entropy. Thus, the notion of ideal glass with zero frozen entropy would correspond to an ideally compacted (to theoretical density) mass of superfine crystalline particles. Would it eliminate the paradox of disordered state of zero configurational entropy[48]?

It appears certain that our understanding of glass transition will widen through inputs related to effects of clustering. Approaches based on treating glasses as disordered solids undergoing a transition on heating[54] or treating viscous supercooled liquids as undergoing transition on cooling[46,48] may prove less profitable in developing a meaningful theory of glass transition.

Magnetic Interactions in Glassy State

Considerable amount of work has been done in recent times on spin glasses[55] in which magnetic atoms are substituted at random in crystalline non-magnetic host lattices. But incorporating magnetic ions such as those of transition metals or rare-earths in non-magnetic glasses provides an interesting situation where both spacial and orientational randomization of spins are present. Studies of such glasses are rather limited and the results reported[56,57] in conventional glasses suggest that the nature

of magnetic interaction is dominantly antiferromagnetic. It has now been found that when the host glass is predominantly ionic, the resultant interactions could be ferromagnetic[58]. In view of the formation of the clusters we discussed earlier, investigation of magnetic interactions in glasses should prove a fruitful and fascinating area of research.

Electron Transport

Last decade has witnessed an unusually large amount of work reported with regard to electron transport in glasses. A large number of glasses studied happen to be chalcogenides. It has now been established that electron transport in chalcogenide glasses should be treated as a distinct category (lone pair semiconductors). The discrepancy in density of carriers indicated from conductivity and ESR (or magnetic susceptibility) studies have led to the current model that transport in chalcogenide glasses occur primarily through charged defects[59,60]. These charged defects correspond to heteropolar scission of bonds and hence to spin paired states. The transport might involve an activated transfer of two electrons[61] (bipolaron mechanism) rather than one. A variety of investigations has been carried out to understand the nature of these defect states, and the present status has been reviewed by Kastner[62].

The formation of defect pairs from under coordinated (with 'broken' bonds) atoms in chalcogenide glasses could very well be thought of as driven by the prospect of energy lowering subject to the constraints of local bonding details. Indeed, by considering an energy minimum principle, it has been found[63] recently that the activation energies for dc transport and minimum energy for creation of a pair of defects are quite comparable Such a comparison implies that the nature of transport involving charged defects possesses characteristics of an intrinsic gap.

There are many areas of research not discussed here which have also provided results of considerable interest such as relaxation spectroscopy[64], pressure effect on semiconducting chalcogenide glasses[65], role of ionicity in glasses[66], etc. But as pointed out earlier, here is only a partial list of trends.

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