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Effects of melt ageing on the density, elastic modulus and glass transition temperature of bismuth borate glasses

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Abstract

Disc shaped samples of the glass composition: $0.40\text{Bi}_2\text{O}_3\text{--}0.60\text{B}_2\text{O}_3$ were prepared by a melt quenching technique by keeping the quenching rate constant but gradually increasing the melt annealing or ageing time from 15 to 220 min at a temperature of 850°C . A total of five glass samples were prepared. Density, ultrasonic velocity and glass transition temperature measurements showed significant changes in the final glass properties. X-ray fluorescence studies confirmed that the glass composition does not change with the heat treatment of the melt. Our findings challenge the conventional theories of liquids and glass formation which predict that structural changes in a low viscosity melt occur almost instantaneously and a liquid is in its internal equilibrium state above the melting point. We report some unusually slow structural relaxations in bismuth borate glass melts even at elevated temperatures of 850°C , due to which the melt transforms from a thermodynamically fragile, high density amorphous state to a low density amorphous state which is kinetically stronger. Our findings indicate that bismuth borate melts are metastable liquids and strong candidates for the phenomenon of liquid state polyamorphism.

1. Introduction

Glasses are non-crystalline materials which have rigidity like solids but have a structure which is indistinguishable from those of liquids. The study of glasses is today a challenging unsolved problem of physics [1–3]. The problem of the nature of glass and glass transition has been called

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the deepest and most interesting problem of condensed matter physics [4]. Conventionally glasses have been prepared by rapidly freezing or supercooling their melts without allowing time for crystallization to intervene. It is a well established fact that the final structure and various properties of glasses depend critically on the quenching rates and composition. In addition, since supercooled liquids and glasses are systems which are not in their thermal equilibrium, their mechanical, optical, thermal, electrical and other properties are not stationary in time but slowly tend toward their equilibrium values when heated to temperatures near the glass transition temperature, T_g . This process is known as structural relaxation or annealing or ageing. However, it has been conventionally believed that the final glass structure and properties do not depend on the time for which the melt has been heat treated at its melting temperature, T_m , much greater than the glass transition temperature, T_g . In other words at temperatures, $T \gg T_g$, the glass melt is considered to be in an internal equilibrium state at any fixed temperature and it is believed that there are no ageing effects in this high temperature region [3]. Recent studies carried out by several investigators challenge the above predictions of conventional theories of liquids and glass formation, at least in the case of borates, which are known to show many anomalies in their structure and properties. It was first reported by Anzai *et al* [5] that there is a variation in density of molten lithium tetraborate with time. Similar effects were observed in sodium triborate glasses [6]. Huang *et al* [7] reported time variation of density, surface tension and viscosity in barium metaborate (BaB_2O_4) melts. Khanna [8] reported a very large dependence of glass density, elastic modulus and visible absorption edge on melt annealing or ageing time in the case of several lead borate compositions. Sabharwal and Sangeeta have reported a very large effect of atmosphere on the crystallization temperature and other thermodynamic properties of calcium, strontium and barium borate melts. They observed that barium borate melt under oxygen is found to supercool down to 966 °C, while under argon the crystallization temperature is further lowered to 887 °C. According to them this novel observation can be used to grow single crystals of barium metaborate by the Czochralski technique [9, 10].

The experimental observations on various borate glass melts, in which the liquid undergoes continuous transformation from a initial high density amorphous (HDA) state to a low density amorphous (LDA) state with the same composition, are very unusual. Up to now they have not attracted the attention that they deserve among glass scientists, although curiously these findings have been observed *in situ* by a few crystal growth researchers attempting to grow single crystals of borates for non-linear optics applications [5, 7]. In this paper the authors have prepared five samples of the glass system: $0.40Bi_2O_3-0.60B_2O_3$ and investigated the effects of melt ageing on the final glass properties, keeping the glass composition and melt quenching rates constant.

2. Experimental details

2.1. Sample preparation

Disc-shaped samples of $0.40Bi_2O_3-0.60B_2O_3$ were prepared by a melt quenching technique. Appropriate amounts of analytical reagent grade Bi_2O_3 and H_3BO_3 were weighed and ground in a mortar and pestle for several hours and heated to 350 °C for 24 h in a porcelain crucible. The crucible was then heated to 850 °C at a rate of 200 °C h⁻¹. The time instant at which the crucible reached 850 °C was taken as $t = 0$. After a few minutes the crucible was taken out of the furnace and a small quantity of the melt was immediately poured onto a heavy brass block kept at room temperature. The glass formed by quenching the melt on the brass block was immediately transferred to an oven where it was annealed at 350 °C for 24 h. The oven was

Table 1. Density, ultrasonic velocity and longitudinal modulus of glass samples as function of melt ageing time.

| Sample no | Melt ageing time (min) | Bismuth concentration (wt%) | Density, d (g cm^{-3}) | Ultrasonic velocity, v (10^3 m s^{-1}) | Longitudinal modulus, L (10^{10} Pa) |
|-----------|------------------------|-----------------------------|-------------------------------------|--|--|
| 10 | 15 | 73.3 ± 1.5 | 5.837 | 3.846 | 8.63 |
| 11 | 45 | 74.6 ± 1.5 | 5.647 | 3.894 | 8.56 |
| 12 | 132 | 73.1 ± 1.5 | 5.165 | 3.962 | 8.10 |
| 13 | 190 | 74.5 ± 1.5 | 5.051 | 3.995 | 8.06 |
| 14 | 220 | 72.9 ± 1.5 | 4.970 | 4.021 | 8.03 |

then switched off and the sample allowed to cool to room temperature at a rate of $35 \text{ }^\circ\text{C h}^{-1}$. The above procedure was repeated five times until the entire melt in the crucible was exhausted. In this way samples of the same composition were prepared by ageing the melt at the same temperatures ($850 \text{ }^\circ\text{C}$) but for different times. The composition and melt ageing times of all the samples are shown in table 1. Also, since the starting temperature was the same and nearly equal amounts of the melt was poured on the same brass block kept at room temperature, the rates of cooling are expected to be same for all samples. These samples were then ground and polished with different grades of emery powders on a soft leather piece fixed on a heavy platform. The grinding and polishing was continued until the sample length measured at the centre and four corners was same within $5 \mu\text{m}$. The final length at the centre was taken as the sample length and used in the ultrasonic velocity measurements.

2.2. XRD and EDXRF analysis of glasses

X-ray diffraction (XRD) studies of all samples were carried out using $\text{Mo K}\alpha$ x-rays (0.71 \AA) on a Rigaku RT 300 C powder diffractometer using Bragg–Brentano reflection geometry. Slits were fixed at 0.5° and a graphite monochromator was placed in the path of the diffracted beam while recording the scattered beam intensity in the 2θ range of 9° – 70° where, 2θ , is the angle of diffraction. XRD investigations confirmed the amorphous nature of all samples. The XRD patterns for all samples are shown in figure 1.

The energy dispersive x-ray fluorescence (EDXRF) analysis of all the five glass samples were carried out for the determination of Bi as well as for the impurities of $Z > 17$ introduced in the preparation of these glasses. To perform the EDXRF analysis, all glass samples were crushed, mixed with cellulose in a 1:1 ratio, prepared in pellet form of mass $\sim 100 \text{ mg cm}^{-2}$ and analysed on an EDXRF spectrometer.

The details of the spectrometer are described elsewhere [11]. A 20 m Ci Cd^{109} radioisotope source was used as an excitation source. The detection system for the energy dispersive measurement consisted of a Si(Li) detector having energy resolution of 150 eV at 5.9 keV and was coupled to an EG&G ORTEC spectroscopy amplifier and multichannel pulse height analyser. The analysis time for all the samples was kept to between 1000 and 5000 s to ensure good statistics for the fluorescence peaks. The net intensities of the various fluorescence peaks were derived using spectrum processing software and non-linear least squares fitting (NL-LSF) procedures. To determine the chemical composition of the glasses, quantitative analysis was performed using a CATXRF quantitative program [12]. The system geometry factor was determined using synthetic standards of several samples including bismuth. A composition analysis was performed on all samples prepared by the above methodology and the Bi weight fraction was determined in each sample by the EDXRF technique. The EDXRF

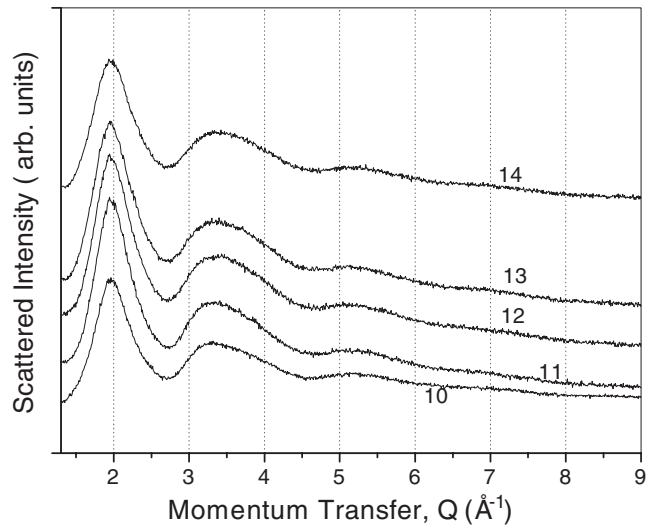


Figure 1. Scattered x-ray intensity as a function of momentum transfer function, Q .

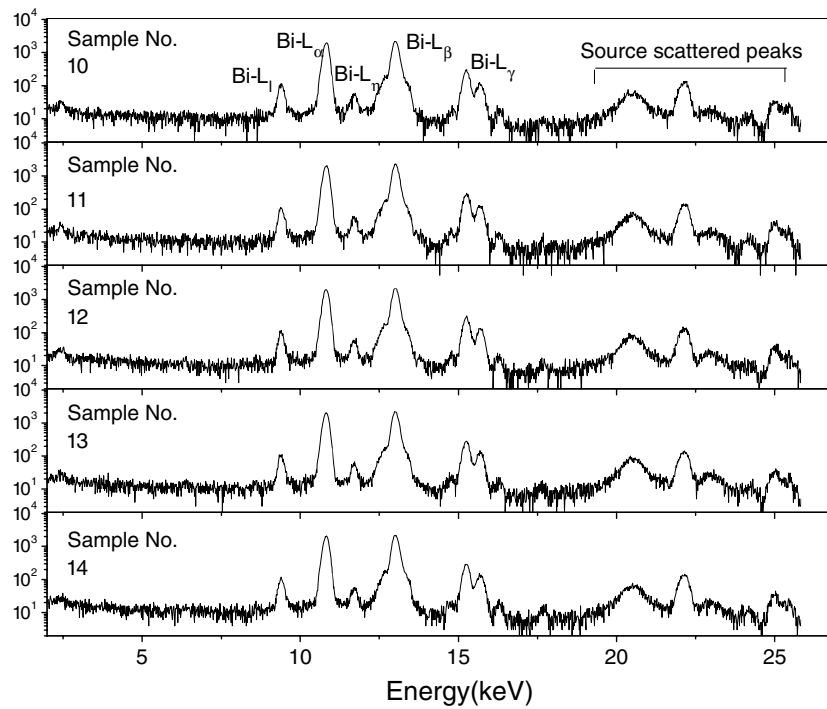


Figure 2. EDXRF spectra for the glass samples.

spectra recorded for all samples are shown in figure 2 and the Bi weight fractions estimated from these studies for each sample are presented in table 1.

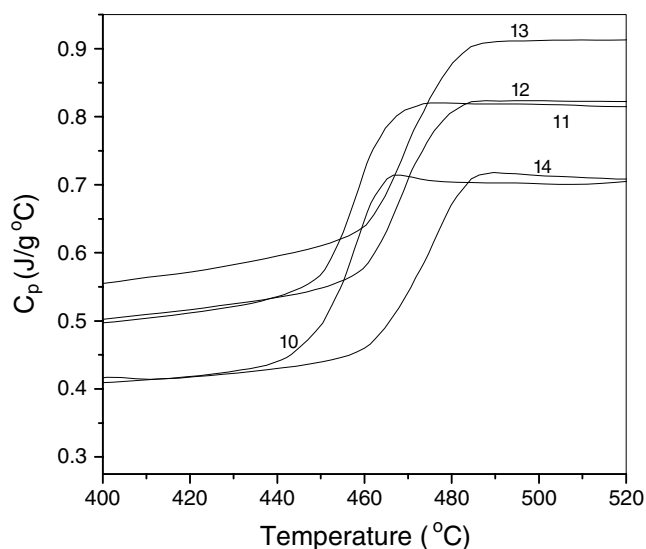


Figure 3. Glass transition in the samples.

2.3. Density, ultrasonic velocity and glass transition measurements

The density, d , of all the glasses at 25 °C was measured by the Archimedes principle using xylene as the immersion fluid.

The ultrasonic velocity, v , was measured in the central part of each disc sample at 5 MHz frequency by the pulse echo overlap technique [13], using an ultrasonic intervalometer (UTI-101, Innovative Instruments, Hyderabad, India). A lead zirconium titanate transducer was bonded to one of the flat faces of each sample using a water based ultrasonic jelly. This technique gave the ultrasonic velocity in the central part of each sample.

The ultrasonic velocity was used to determine the longitudinal modulus, L , by the following relationship:

$$L = v^2 d. \quad (1)$$

The glass transition temperature, T_g , was measured in all samples using a temperature modulated differential scanning calorimeter (TA Instruments, Model 2910). All samples were heated at the same rate of 10 °C min⁻¹ and the glass transition temperature, T_g , was taken as the point of inflection in the specific heat capacity curves shown in figure 3. The specific heat capacity (mass normalized heat capacity) was calculated from the reversible heat flow measurements. The DSC measurements in each sample were repeated several times and the precision and accuracy of T_g calculated for each sample is ± 1 °C. The excess or jump in specific heat capacity, ΔC_p was calculated from the step transition in the heat capacity [14]. The width of the glass transition, ΔT , was taken as the difference between the end point and onset point of the step transition in heat capacity, while the slope, m , of the glass transition was defined as:

$$m = \Delta C_p / \Delta T. \quad (2)$$

The values of these thermodynamic properties in all samples are presented in table 2.

Table 2. Thermodynamic properties of glasses.

| Sample no | T_g (°C) | ΔC_p (J g ⁻¹ °C ⁻¹) | ΔT (°C) | m |
|-----------|------------|--|-----------------|--------|
| 10 | 455 | 0.28 | 15 | 0.0186 |
| 11 | 458 | 0.30 | 16 | 0.0187 |
| 12 | 470 | 0.28 | 17 | 0.0164 |
| 13 | 470 | 0.29 | 22 | 0.0132 |
| 14 | 474 | 0.28 | 23 | 0.0122 |

3. Results and discussion

It can be seen from table 1 that the glass density shows a large decrease with melt ageing time. XRD studies carried out on all samples provide some insight into the possible reasons for these changes. Figure 1 shows the XRD patterns for all samples after applying the background and polarization corrections to the data as a function of the momentum transfer parameter, $Q = 4\pi \sin \theta / \lambda$. While here we report only preliminary XRD studies, carried out to confirm the amorphous nature of the samples, some conclusions can be drawn from these studies about the effects of melt ageing on the structure and properties of bismuth borate glasses. Firstly similarities in the diffraction spectra for all samples show that the differences between them are structural rather than compositional. The XRD patterns mostly reveal the Bi–Bi, Bi–O and Bi–B correlations rather than the B–O and O–O correlations that exist in the glass network, due to the much larger x-ray scattering power of Bi atoms. We observe a first sharp diffraction peak (FSDP) centred around $Q = 2.0 \text{ \AA}^{-1}$ in all samples. The relative intensity of the FSDP increases with the decrease in sample density, i.e. as we move from sample 10 to 11. These experimental observations of the increase in relative intensity of FSDP with decrease in glass density are consistent with the recent ideas that the FSDP in glasses is a mid-range order (MRO) peak that scales with the amount of void volume around the cation centred units in the glass network [15–19]. These observations show that the effects of melt ageing are greater in the MRO or in the structural arrangements existing at distances in the range 5–10 Å in the glasses, and that it may be more informative to carry out x-ray and neutron diffraction studies in the low- Q region.

It can be seen in table 2 the glass transition temperature increases while the density and longitudinal modulus decreases with melt ageing time (table 1). A straightforward explanation for these property changes could be attributed to the selective loss of constituents from the melt on its heat treatment. It is known that the decrease of Bi₂O₃ concentration in bismuth borate glasses leads to a decrease in density and an increase in glass transition temperature [20]. Figure 2 shows the EDXRF spectra for all samples. These spectra are exactly identical, indicating that the composition of all glasses is the same. A quantitative analysis carried out on the EDXRF spectra showed that the Bi weight fraction is same in all samples within the limits of experimental error, thus ruling out any selective evaporation of Bi₂O₃ from the melt. The boron and oxygen content could not be estimated by our EDXRF spectrometer but if there had been any selective evaporation of B₂O₃ from the melt it would have led to a gradual increase in the concentration of Bi weight fraction and consequently an increase in glass density. The opposite observations of decreasing glass density with ageing time indicates that there is no selective evaporation of the constituents from the melt instead there are some unusually slow structural rearrangements occurring in the bismuth borate melt at temperatures well above its melting point. The melt expands very slowly with time and is not in its internal equilibrium state during the time period investigated in this paper. Our findings challenge the conventional viewpoint that the glass melt is in its internal equilibrium state at any temperature, $T \gg T_g$ [3].

It was suggested by Huang *et al* that the following structural transformations:



where \emptyset represents a bridging oxygen and O^- a non-bridging oxygen (NBO), take place slowly in the borate melt and are responsible for the changes observed in various glass properties as a consequence of the time effect [6]. $B\emptyset_2O^-$ units are estimated to have a volume about 1.70 times more than that of $B\emptyset_4^-$ units by the NMR studies carried out by Karki *et al* [21]. Earlier Khanna also attributed the effects of melt annealing on the properties of lead borate glasses to the above mechanism [8]. However an increase in glass transition temperature with ageing time, as observed in the present glass system indicates there are other, more dominant mechanisms taking place very slowly in the bismuth borate melt which lead to large changes in various glass properties. If the breaking up of boron tetrahedral units, $[B\emptyset_4]^-$, into triangular boron units, containing two bridging and one NBO, $B\emptyset_2O^-$, had been the only transformation occurring in the melt, the glass transition temperatures should have decreased drastically [22]. Our experimental observations of increase in glass transition temperature shows that there is an increasing network connectivity as a consequence of the time effect. The increase in network connectivity increases the glass transition temperature as recorded by our DSC measurements.

Although we see a large increase in glass transition temperature, the excess specific heat capacity remains nearly constant while the width of glass transition shows a systematic increase with melt ageing time. These changes show that the fragility of the bismuth borate melt, which is classified as a highly 'fragile' glass former by Angell's classification scheme of liquids, is changing with melt ageing time. In fact a large but nearly constant excess or jump in specific heat capacity value, ΔC_p , and a systematic decrease in the slope of glass transition, m , indicates that although the liquid is becoming kinetically stronger it is thermodynamically still very fragile [26].

Similar 'time effect' observations were reported earlier in lithium tetraborate melts and sodium triborate glasses, but the decrease in glass density with melt ageing time of several hundred minutes was only about 0.3% in these two glass systems [5, 6]. However larger effects were reported in barium metaborate (BaB_2O_4) melts by the *in situ* measurements carried out by Huang *et al*. These authors reported a decrease in the density of BaB_2O_4 melt by nearly 1.5% over a melt ageing time of 600 min at a temperature of 1087 °C [7]. Khanna earlier reported a very large decrease in the density of lead borate glasses in the range of 3–5% over a melt ageing time of few hours at 900 °C [8]. It seems that the slow structural relaxation is a fundamental property of borate melts and the changes observed in melt properties by slow ageing process gets enhanced in the presence of heavy metal atoms like Ba, Pb and Bi, which are known to act as network formers at large concentrations. It was suggested earlier by Uchida *et al*, on the basis of their hard and soft acids and bases (HSAB) theory [26, 27], that hard alkali metal cations like Li^+ , Na^+ , etc, are stabilized around tetrahedral boron units, $[B\emptyset_4]^-$, which worked as a rather hard base, while soft acidic cations such as Pb^{2+} , Bi^{3+} and Sn^{2+} are stabilized around $B\emptyset_2O^-$ units which act as a rather soft base. This has been supported by NMR and x-ray photoelectron spectroscopic studies carried out by Hayashi *et al* on $SnO-B_2O_3$ glasses [28]. Thus tetrahedral boron units are inherently unstable in the presence of ions like Pb^{2+} , Bi^{3+} and break into much larger metaborate triangular units, $B\emptyset_2O^-$. It is known that Bi_2O_3 is an intermediate and can act as network formers at high concentrations [29]. In addition, it is known that while acting as network formers both Pb and Bi atoms tend to form links with triangularly co-ordinated boron units rather than tetrahedral boron units [30]. Thus some co-operative structural rearrangements are lowering the melt and glass density with ageing time. Because of their ability to act as network formers, Pb and Bi atoms can participate in the co-operative structural rearrangements, occurring in the glass melt, to a greater extent

and therefore 'time effects' produce a very large changes in density and other properties of the final glasses. Since Li and Na ions can only act as network modifiers, their co-operation in structural rearrangement is very limited and consequently there is a much smaller melt ageing effect in these glasses [5, 6].

An important question that arises is that if the tetrahedral boron units are inherently unstable in the presence of heavy metal atoms like Bi at high temperatures, why is it that to start with we have a large concentration of these units in the melt which then slowly degrade into larger and more stable triangularly co-ordinated boron units with melt ageing? This can be understood from the studies carried out by other investigators on lithium borate glasses and melts. Earlier Chryssikos *et al* studied the devitrification and polymorphism behaviour of lithium metaborate (LiBO_2). These authors successfully obtained three different crystalline polymorphs of LiBO_2 by the ambient pressure devitrification of glassy lithium metaborate (g-LiBO_2) [31]. In particular they prepared two crystalline polymorphs $\alpha\text{-LiBO}_2$ and $\gamma\text{-LiBO}_2$ by the isothermal, ambient pressure heat treatment or annealing of g-LiBO_2 . $\alpha\text{-LiBO}_2$ contains only triangularly co-ordinated boron atoms and could be obtained by the annealing of g-LiBO_2 at temperatures in the range $450^\circ\text{C} < T < 850^\circ\text{C}$. The annealing of g-LiBO_2 at $T < 400^\circ\text{C}$ produced $\gamma\text{-LiBO}_2$, which contained only tetrahedral boron units. These authors concluded that tetrahedral boron units are more stable in borate glasses at temperatures, $T < 400^\circ\text{C}$ whereas at high temperatures they tend to transform to triangularly co-ordinated boron units. These experimental findings by Chryssikos *et al* provide an answer to our previous question as to why to start with we have tetrahedral boron units, $[\text{B}\emptyset]_4^-$, in bismuth borate melts although these are unstable at high temperatures especially in the presence of heavy atoms like Bi and Pb.

$[\text{B}\emptyset]_4^-$ units in the melt are actually the remnants of the previous sintering of starting batch crystalline materials at about 400°C before melting. Earlier Krogh-Moe had proposed a useful model of borate glasses which predicts that these glasses are made up of randomly connected superstructural groups, similar to those found in their crystalline compounds [32]. These ideas are supported by techniques like infrared [33, 34], nuclear magnetic resonance [35] and Raman spectroscopy [36]. We believe that low temperature crystal-like entities or superstructural groups like pentaborate, di-pentaborate, di-borate, triborate, etc, each of which contain one or more tetrahedral boron units, persist in the bismuth borate melts even at high temperatures of 850°C , and very slowly disappear on its heat treatment by some co-operative structural rearrangements. These conclusions are consistent with Brazhkin's phenomenological theory of crystal-amorphous phase changes which predict the existence of long lived crystal-like clusters in the liquid [37]. New evidence that borate melts have indeed a memory of their previous history is provided by the recent DTA measurements carried out by Sabharwal *et al* [38] to study the crystallization behaviour of lithium triborate (LiB_3O_5). These authors discovered that the highest temperature has a large effect on the crystallization of LiB_3O_5 melts. DTA measurements carried out on LiB_3O_5 melts, when the highest temperature was limited to few degrees ($<23^\circ\text{C}$) above its melting point (837°C), showed crystallization exotherms in DTA cooling curves. However, when the LiB_3O_5 melt was overheated to 900°C for 1 h and then a DTA plot was recorded during the cooling cycle, the crystallization exotherm was absent. This showed that the heat treatment of the melt to 900°C inhibited subsequent crystallization on cooling and the borate liquid has a memory of its previous thermal history.

The transition of the bismuth borate melt on its ageing from the initial HDA state to a LDA state indicates that bismuth borate and other borate liquids are metastable liquids just after melting, and their structural relaxation as observed by us is of an entirely different mechanism compared with the conventional structural relaxation exhibited by a metastable solid like glass when the later is aged or annealed at a temperature less than its glass transition temperature, T_g . When a metastable solid like glass is aged at a temperature, $T < T_g$, it always relaxes

to a state of higher density and lower fictive temperature [39, 40]. On the contrary the heat treatment or the ageing of the bismuth, lead, barium, sodium and lithium borate melt always causes a decrease in its density. While the structural relaxation of glass on its ageing only takes it from one potential energy minima to another without altering its potential energy landscape, the structural relaxation of a bismuth borate melt is different in the sense that the potential energy landscape of the liquid is itself changing by co-operative bond rearrangements. Our DSC results (table 2) seem to indicate that the liquid's potential energy landscape is getting modified in such a way that although the total number of potential energy minimas remain nearly constant, their barrier heights are increasing. Hence, although the liquid retains its high thermodynamic fragility with ageing time, it is kinetically becoming stronger and it becomes increasingly difficult for the liquid to go from one potential energy minima to another due to rise in potential barrier heights [26].

An important conclusion that we arrive at from our studies is that a liquid like bismuth borate melt cannot be described by a single parameter like density as has been conventionally accepted for liquids. This common sense view needs to be rejected. Rather there must be other parameters that need to be determined for describing the liquid structure and its properties completely. Such a two-parameter, Landau model of liquids has recently been proposed by Tanaka [41]. According to Tanaka a new additional bond-order parameter, which favours spontaneous formation of locally favoured structures needs to be taken into consideration for describing the liquid structure and its various properties completely. According to this picture a liquid in general favours two different types of symmetry: one that maximizes density, while the other maximizes the quality of local bonds, also the symmetry of the latter is not consistent with the crystallographic symmetry of the former and therefore the increase in the bond-order parameter will inhibit crystallization. Moreover the formation of locally favoured structures always leads to a decrease in density. We believe that the heat treatment of the bismuth borate melt leads to the formation of these locally favoured structures, which also leads to the decrease in melt density. The formation of these locally favoured structures inhibits crystallization and explains why the overheating of $\text{Li}_3\text{B}_2\text{O}_5$ melts to 900°C for one hour prevented subsequent crystallization on cooling as observed recently by Sabharwal *et al* in their DTA studies [38]. Ageing of the borate melts at high temperatures slowly modifies the crystal-like entities or superstructural groups that exist in it. There is an increase in short range bond ordering which also simultaneously lowers the melt density. Recent computer simulation studies carried out in liquid water also show that low density regions can arise due to some co-operative structural rearrangements [42]. In a more recent study Tanaka has found a direct relationship between the short range bond-ordering parameter and the fragility of the glass forming liquid: an increase in the short range bond-ordering parameter is found to decrease the liquid's fragility index [43]. Fragility can also be defined as the measure of degree of co-operativity in atomic motion [43]. Bismuth borate melts are highly fragile glass forming liquids because of the large co-operativity in atomic rearrangements, which in turn leads to the large decrease in the melt's density on ageing.

Tanaka has further used his two order parameter theory of liquids to explain the highly intriguing phenomenon of liquid-liquid separation and polyamorphism [41, 44, 45]. Here by the term phase separation we refer to the unusual and rather mysterious separation of a liquid into components with the same composition but different structures and thermodynamic properties. Polyamorphism is the amorphous analogue of the well known phenomenon of polymorphism exhibited by many crystalline elements and compounds. In the strictest sense polyamorphism refers to the phenomenon by virtue of which a condensed non-crystalline substance like a liquid or a glass can exist in distinct states having different thermodynamic properties and structures but identical composition [3, 46–51]. The first established and

well characterized cases of polyamorphism in glasses was probably in amorphous ice as discovered by Mishima *et al*. These authors discovered that vapour deposited, LDA ice could be reversibly transformed to a HDA ice in an apparently narrow pressure range at temperatures of ~ 130 – 150 K [52, 53]. It was also found that if HDA ice is warmed to 113.4 K it suddenly expands to LDA ice. This provided the direct evidence for the existence of polyamorphism in amorphous H_2O . A narrow pressure and temperature range in which the LDA \longleftrightarrow HDA transformation was observed was further believed to indicate that polyamorphism in H_2O is a first order phase transition which occurs at a rather sharp temperature and or pressure change rather than a continuous structural relaxation phenomenon [54–56]. But these views about the phase transition in amorphous ice have been challenged by the recent neutron and x-ray scattering experiments carried out by Tulk *et al* [57]. These authors were able to obtain several distinct metastable states of amorphous ice by the ageing of HDA ice at temperatures much less than 113.4 K, the temperature at which the transition from HDA form to LDA form is known to occur suddenly. These recent studies suggest that polyamorphism may be a structural relaxation phenomenon rather than a true phase transition [58–60]. It is perhaps a new kind of smeared out phase transition which occurs over a range of temperatures and pressures as has been observed in some of the chalcogenide melts [61, 62]. The most dramatic example of polyamorphism in glasses is probably the discovery of density driven liquid–liquid phase separation in the supercooled melt of Al_2O_3 – Y_2O_3 by Aasland and McMillan [63]. These authors showed by microscopy the coexistence of two liquid phases in the Al_2O_3 – Y_2O_3 system which have identical composition but different density, structure and thermodynamic properties [64–66]. Another known candidate for liquid state polyamorphism is tri-phenyl phosphite [67–71].

It is clear from the experimental results presented in this paper that the structure and properties of bismuth borate, just after melting, is quite different from that of the melt which has been molten for a long time, and that the liquid reaches its equilibrium state very slowly in time and not instantaneously as predicted by conventional theories of glass formation. There is a continuous transition of the bismuth borate liquid from a highly fragile, HDA state to a LDA state with lesser fragility by its slow structural relaxation. Both the amorphous states have the same composition but have different structure and properties. Thus bismuth, lead, barium and other borate melts are metastable liquids and are strong candidates for the intriguing phenomenon of liquid state polyamorphism.

Further, while ambient pressure, high temperature ageing causes slow structural relaxation, it is quite possible that at high pressures and temperatures we may see an abrupt transition of the bismuth borate liquid from one amorphous state to another distinct, metastable amorphous state as has been observed recently by Katayama *et al* in molten phosphorus [72]. Such liquid–liquid phase transitions are believed to occur in liquid carbon [73]. It would be equally interesting to see if there is any ‘time effect’ in the density and structure of molten phosphorus and Al_2O_3 – Y_2O_3 melt, or in other words explore the possibility of ageing in these two substances as observed by us in bismuth borate melts and more recently in amorphous ice by Tulk *et al* [57].

Our findings reveal that various properties of bismuth and other heavy metal oxide borate glasses, which find application as non-linear optical materials [74–76], can be tailored simply by freezing the borate melt at different times in its ageing period without altering the other critical parameters like the quenching rate and glass composition. Interestingly, Martin *et al* [77] have recently demonstrated the tailoring of properties and structure of some ZnCl_2 based glasses by designing intermediate or MRO in these amorphous materials.

4. Conclusions

We conclude that the structure and the properties of bismuth borate melt evolves slowly with time and the melt is not in its equilibrium state immediately after melting. Due to slow cooperative structural rearrangements in the melt, it transforms continuously from a HDA state to a LDA state with the same composition. The heat treatment or the ageing of the bismuth borate melt at constant temperature and pressure, changes the potential energy landscape of the liquid such that although the density of potential energy minimas do not change, their relative barrier heights increase and it therefore becomes more and more difficult for the liquid to go from one potential energy minima to another. Bismuth borate and also other borate melts are metastable liquids and show liquid–liquid phase transformations on their ageing. Our findings indicate that it is possible to tailor the physical properties of bismuth borate glasses by altering the melt history without changing the other critical parameters like quenching rates and glass composition. The chemical durability of the glasses prepared from the melt with different ageing history are also expected to be different.

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