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Effects of annealing on density, glass transition temperature and structure of tellurite, silicate and borate glasses

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ABSTRACT

Barium tellurite, lead tellurite, molybdenum tellurite, lead silicate and bismuth borate glasses of the compositions: xBaO-(100-x)TeO_2 (x = 10, 15 and 20 mol%), xPbO-(100-x)TeO_2 (x = 15 and 20 mol%), 25MoO_3-75TeO_2, xPbO-(100-x)SiO_2 (x = 50, 60 and 65 mol%) and 40Bi_2O_3-60B_2O_3 were prepared by melt-quenching. The effects of long duration thermal annealing (below the respective glass transition temperature (T_g) values) on the density, thermal properties and the short-range structure of glasses were studied. Density increases on average by about 0.5% to 1% and T_g values show drastic increase in the range of 8 °C-64 °C after annealing. Raman and FTIR studies were performed on glasses before and after annealing, FTIR studies found that bismuth borate glasses show a small but significant increase in the fraction of tetrahedral borons in the borate network with annealing. Raman studies on lead metasilicate glass showed an increase in the concentration of SiO_4 units that contain three bridging oxygens. Raman and FTIR spectra of all annealed barium and lead tellurite glasses were indistinguishable from those of the initial samples, however the FTIR spectra of annealed 25MoO_3-75TeO_2 glass show changes in the relative intensities of the peaks due to Mo—O vibrations along with the growth and sharpening of low frequency Raman bands, furthermore this glass also showed large differences in its crystallization and melting properties during thermal analysis.

1. Introduction

Glass is an amorphous (non-crystalline) solid that has atomic structure indistinguishable from that of a liquid. Glass structure is complex, due to the lack of long-range order of the constituent atoms/ions, but glasses have definite short-range order. The study of nature of glasses and the phenomenon of the glass transition remains a challenging, unresolved and intriguing problem of condensed matter physics [1,2]. When a glass is fabricated, the material is rapidly cooled from its liquid state till its temperature drops below it's melting or freezing point. At this stage, the material is a supercooled liquid, an intermediary, transient phase between the liquid and glass states. To become an amorphous solid or glass, the material is cooled further, below the glass-transition temperature [3]. Moreover, supercooled liquids and glasses are non-equilibrium states of matter; their mechanical, optical, thermal, electrical and other properties are not stationary in time but slowly and gradually approach toward their equilibrium values when glasses are heated at temperatures below the glass transition temperature, T_g. This phenomenon, which changes properties of glasses, is known as the structural relaxation or ageing [4]. The relaxation of thermodynamic properties, e.g., volume or enthalpy, with annealing time and temperature is a known as structural recovery. Studies of relaxation phenomena in glasses are profoundly interesting because it reveals modifications in the atomic structure of disordered solids and their correlations with the thermal, optical and mechanical properties [5–7]. For any glass, the value of T_g provides information on the strength of interatomic bonds and on the network connectivity, similar to the relationship of melting temperature with chemical bonding strength in crystals.

Ma et al. [8] reported that the enthalpy will slowly relax to the equilibrium value, when tellurium chalcogenide glasses are isothermally annealed at temperature, T, below their T_g values. Thermal studies on $Te_{33}Se_5Br_2$ glass (T_g = 71 °C) were carried out on as-formed glass (without annealing) and after several days of annealing treatment at a temperature of 20 °C and it was found that sub-T_g isothermal annealing produces drastic increase in the glass transition temperature.

During annealing, the fraction of non-bridging oxygens in oxide glasses is likely to decrease with the simultaneous formation of bridging

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oxygens which fills the voids as a result of which a more compact or densely packed network is produced. Long duration heat treatment of glasses may possibly decrease the degree of disorder or some voids may be removed from the network [9–11]. By increasing the ageing time, the glass transition endotherm (change in baseline) is reported to become more pronounced [12]. The influence of isothermal annealing was comphrenhensively studied in polymer glasses by Volynskii et al. [13] and in poly DL-latide by Kairong et al. [14], it was found that as the annealing time increases the glass transition-endothermic peak becomes more sharp or prominent. The effects of annealing time at constant annealing temperature shows remarkable and very intriguing changes in the density, and optical properties of glasses. It is well known that annealing treatment of silica glasses profoundly effects the loss factors for optical fiber applications [15,16].

Tellurite, silicate and borate glasses are of great scientific and technological importance for their applications in fiber optics, laser hosts, infrared to visible upconversion, applications in optical data storage, sensors, laboratory glassware, reflecting and transmitting windows, and for non-linear optical devices [17–19]. B_2O_3 and SiO_2 are excellent glass formers which form glassy phases easily even at very low melt-quenching rates, on the contrary, TeO_2, is an conditional glass former which forms glass in the pure form at high melt-quenching rate of $\sim 10^5\,K\,s^{-1}$ [20]. TeO_2 however forms variety of binary and ternary glasses at moderate quenching rates of 10^2 to $10^3\,K\,s^{-1}$ when it is mixed with alkali, alkaline-earth, heavy metal and transition metal oxides [21,22]. Borate and tellurite glasses have many attractive properties over the silicate glasses. While silicate glasses have all silicon ions in tetrahedral coordination [22,23], the boron and tellurium ions in the borate and tellurite network respectively, have a dual co-ordination numbers of 3 and 4 with oxygens [24,25]. The addition of modifier metal oxides in borate and tellurite network produces changes in B—O and Te—O speciation and influences the glass forming ability of materials [26,27]. In case of tellurite glasses TeO_4 transform into TeO_3 units with increase in metal oxide content [28,29].

There is close connection between physical ageing/relaxation and the glass transition phenomenon. To understand the glass transition problem, the full understanding of the structural relaxation (α-relaxation and β-relaxation) and its dynamics are necessary [30]. It is found that the relaxation behavior in amorphous solids can be well described by the Kohlraush-Williams-Watts (KWW) relaxation function above and below T_g [31,32].

$$\phi(t) = \exp.[-(t/\tau)^{\beta}] \quad (1)$$

where τ is characteristic relaxation time and $\beta = (1\text{-}n)$ is the fractional exponent.

The relaxation process is generally studied by mechanical or dielectric spectroscopy in wide temperature ranges. The α-relaxation prominently appears in the dielectric spectra [33]. The α-relaxation is observed above the glass transition temperature at high frequencies, however on moving toward lower frequencies and with lowering of temperature, the secondary relaxations dominate the dielectric spectra. The α-relaxation is slowed down upon cooling as the glass transition temperature T_g is approached. Secondary relaxation mainly depends upon the thermodynamic properties of glass [34]. Different types of motions that influence the molecular arrangement of glass like localized instability of the whole molecules, or the rotational instability of the side groups, give rise to the secondary relaxation. According to Johari and Goldstein, the secondary relaxation which is a universal feature of glass forming materials occurs in rigid, molecular glass-formers devoid of intramolecular degrees of freedom [35–37]. According to Vyazovkin [38], by increasing the time of annealing, the endothermic glass transition peak shifts to higher temperatures. Chen [39] found that, when metallic glass, $Pd_{48}Ni_{32}P_{20}$ is annealed for 210 h below T_g, the whole curve for C_p Vs T shifts toward higher temperature relative to the reference one with the simultaneous large increase in the T_g value.

There are several reports on the effects of sub-T_g annealing on the properties of chalcogenide, organic, polymer and metallic glasses [8,13,14,35,36,39], however there are only few studies on the effects of annealing/ageing on the structure and properties of oxide glasses which have wide range of applications [5,6,15,16]. It is the objective of the present study to understand the effects of long duration annealing treatment (below the respective T_g values) of some heavy metal oxide tellurite, silicate and borate glasses and correlate the changes in the density and thermal properties with the changes in short-range structure. Raman and Fourier Transform Infrared (FTIR) spectroscopies are used to determine the changes in short-range structure, while thermal properties are analyzed by Differential Scanning Calorimetry (DSC).

2. Experimental

Barium tellurite, lead tellurite, molybdenum tellurite, lead silicate and bismuth borate glasses of the composition: $xBaO\text{-}(100\text{-}x)TeO_2$ (x = 10, 15 and 20 mol%), $xPbO\text{-}(100\text{-}x)TeO_2$ (x = 15 and 20 mol%), $25MoO_3\text{-}75TeO_2$, $xPbO\text{-}(100\text{-}x)SiO_2$ (x = 50, 60 and 65 mol%) and $40Bi_2O_3\text{-}60B_2O_3$ were prepared by melting appropriate amounts of analytical reagent grade chemicals (PbO, SiO_2, Bi_2O_3, MoO_3, $BaCO_3$, H_3BO_3 and TeO_2) in a platinum crucible. The starting chemicals were mixed and ground in an agate mortar pestle for about 30 min and then transferred to a platinum crucible. Disk shaped samples were prepared by normal quenching; in this method, the melt was poured on a brass block and a disk shaped glass was prepared and immediately transferred to another furnace where it was annealed for about half an hour at temperatures below their respective glass transition temperatures to reduce thermal stresses that are generated by rapid cooling. Normally quenched samples are labeled as “N”.

Lead metasilicate and bismuth borate glass samples were also fabricated by splat quenching; in this method small quantity of the melt was pressed between two metal plates. The splat-quenched samples are

Table 1
Composition, density, glass transition temperature (T_g) of barium tellurite, lead tellurite and molybdenum tellurite glasses. Samples with label “H” denote the glasses with long duration annealing treatment.

Sample code	Composition (mol %)	Annealing temperature (°C)	Annealing time (h)	Density, d ($g\,cm^{-3}$)	(T_g) (°C) (± 1°C)
10BaTe	$10BaO\text{-}90TeO_2$	250	0.5	5.582 ± 0.002	321
10BaTe-H			1920	5.614 ± 0.001	331
15BaTe	$15BaO\text{-}85TeO_2$	250	0.5	5.561 ± 0.001	326
15BaTe-H			1920	5.587 ± 0.001	341
20BaTe	$20BaO\text{-}80TeO_2$	250	0.5	5.521 ± 0.001	335
20BaTe-H			1920	5.564 ± 0.001	343
15PbTe	$15PbO\text{-}85TeO_2$	250	0.5	6.042 ± 0.002	291
15PbTe-H			1626	6.111 ± 0.002	306
20PbTe	$20PbO\text{-}80TeO_2$	250	0.5	6.199 ± 0.002	284
20PbTe-H			1626	6.268 ± 0.002	299
25MoTe	$25MoO_3\text{-}75TeO_2$	250	0.5	5.256 ± 0.004	320
25MoTe-H			1082	5.302 ± 0.007	343