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Characterization of Pr₆O₁₁-Ag₂O-B₂O₃ Glasses

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Abstract

Silver borate glasses doped with Praseodymium of different concentration has been prepared by melt quench technique. X-ray diffraction pattern shows that there is no sharp peak it confirms the amorphous nature of the present glasses. The glass transition temperature (T_g) of this glass system have been studied using the Matic MBS-8000 Digital Signal Processing and Conventional Thermal Analysis (DTA) method. The T_g of these glasses increases with increase in concentration of Pr₆O₁₁ except at 0.2 mol% T_g value is lower. We investigate the network structure of Pr₆O₁₁-Ag₂O-B₂O₃ glass by ¹¹B magic angle spinning (MAS)-nuclear magnetic resonance (NMR) which shows the presence of sharp peak at around 18 ppm. Formation of B₄ units is assumed to be occurring initially through the formation of oxygen bridges between [BO_{3/2}]⁰ units in B₂O₃.

Keywords: Silver borate glass, Praseodymium, XRD, DTA and MAS-NMR.

Introduction

B₂O₃ based glasses have been widely studied over the past decades due to their technological applications and for understanding the structural particularities as the occurrence of boron anomaly. Today, borates are important materials for insulation (glass wool) and textile (continuous filament) fiberglass [1]. Borate glasses are host of widespread optical, electrical, magnetic and other technologically interesting properties [2]. Borate glasses present very interesting features such as optically transparency from the visible to the near infrared range, wide compositional regions, resistance against devitrification, high refractive index and density [3]. For the past few years, metal oxide glasses are being intensively studied due to their optimal properties for photonics [4]. Silver borate glasses in particular have attracted a lot of attention because of their high ionic conductivity, resistance against humidity and possibility of being used in large number of fields such as biomaterials [5]. This property makes a basis for their applications in electrochemistry as solid electrolytes [6]. The optimization of such properties requires a good knowledge of the microscopic glass structure. In particular, a

deeper knowledge of the local environment of the moving ions is highly desirable [7].

Pure boron oxide B₂O₃ in the glass state consists of three coordinated boron atoms, which can be associated to form six-member boroxal rings [8]. Silver is generally present as a network modifier, above 27 mol % Ag₂O some atomic silver is assumed to be present and below 15 mol % Ag₂O exploratory studies indicate a two phase structure within an immiscibility gap [7-8]. The oxides of praseodymium represent a system of phases whose composition is variable, although being restricted to a well defined range and whose structure may be extensively defective. In addition to Pr₂O₃ and PrO₂, at least other five sub oxide phases have to be taken into consideration and they represent a series of homologues having the Pr_nO_{2n-2} general composition. Among the different phases, Pr₆O₁₁ is the stable one at room temperature in air [9]. Praseodymium oxide (Pr₆O₁₁) doped crystals and glasses have proved to be effective for several applications in optical devices [10].

The ¹¹B Magic Angle Spinning (MAS)-Nuclear Magnetic Resonance (NMR) investigation studies were important in identifying several borate groups consisting of

boron oxygen triangles and tetrahedra which form the glass network at various modification levels [11-15]. The nature and the amount of modifier oxide influenced the concentration of borate species which appear in the glass structure.

In this chapter, we present the characterization of praseodymium oxide doped silver borate glass system and investigate the influence of silver oxide (Ag_2O) and Praseodymium oxide (Pr_6O_{11}) on borate glass network by means of XRD, DSC and MAS-NMR techniques. The results were discussed in view of change in structure of borate glass network.

Experimental Techniques

Glasses were synthesized having a general formula $(25-x)\text{Ag}_2\text{O}-75\text{B}_2\text{O}_3$ ($x=0$) which is base glass system and praseodymium oxide doped glasses were also synthesized having a general formula $x\text{Pr}_6\text{O}_{11}(25-x)\text{Ag}_2\text{O}-75\text{B}_2\text{O}_3$ ($x=1,2,3,4$ mol %). The starting materials are the analar quantity of boric acid (H_3BO_3), silver oxide (Ag_2O) and Praseodymium oxide (Pr_6O_{11}) used in the preparation of glasses. Table 1 lists the batch composition in mole % of glasses studied in the present work. The chemicals were weighed accurately in an electronic balance and ground to fine powder and mixed thoroughly. The batches were then placed in porcelain crucibles and melted in an electrical furnace at around 1200°C . To obtain homogeneity, the melt was stirred frequently. The melt was then quenched between two copper blocks from a high temperature to room temperature (303 K). After quenching all the samples were immediately transferred to an annealing furnace. Samples were annealed at 250°C for 1 hour in order to relax strains present in quenched glasses during sudden quenching. The glass samples were stored in desiccators to prevent from moisture.

X-ray diffraction is used to identify the crystalline or amorphous/glassy nature of the synthesized samples. Philips X'pert pro powder X-ray diffractometer with Cu anode K_α radiation of wavelength $\lambda = 1.54439 \text{ \AA}$ is used to record X-ray diffraction patterns for all compositions of prepared glass samples for 2θ values 10° to 70° at a scan rate of 2° per minute with 2000 counts per second. Fine powdered sample of each composition is

pressed tightly in a sample holder to form a plane surface and loaded on the platform to record XRD patterns.

DSC is used to identify the thermal behaviors, especially, glass transition temperature (T_g) of the materials. The DSC is measured by using the instrument Netzsch Simultaneous Thermal Analyzer STA409C with 32. The fine powdered sample of ~ 7.5 mg is placed in the aluminum pan with lid and pressed to form a thin button like micro pellet. The prepared micro pellet sample is subjected to heat at the rate of 10 Kmin^{-1} from $323 - 823$ K under the nitrogen atmosphere and recorded the DSC curves using a Mettler Toledo star^e system module: DSC: SW-9.30.

^{11}B Magic Angle Spinning (MAS)-Nuclear Magnetic Resonance (NMR) were recorded using a bruker MSL-300 solid state high resolution spectrometer. It is operating at 96.28 MHz with a magnetic field of 7.05 Tesla. A 90° pulse with duration of 5 μsec and a pulse delay of 5 μsec was employed. A cylindrical zirconia rotor with spinning speed of 3000-4000 Hz was used in all experiments. All the spectra were recorded at room temperature using freshly powered samples.

Results and Discussion

Figure 1 shows X-Ray Diffraction patterns of the present $\text{Pr}_6\text{O}_{11}-\text{Ag}_2\text{O}-\text{B}_2\text{O}_3$ glass samples. All the glass samples were found no discrete or continuous sharp peaks, but broad halo at around $22^\circ - 32^\circ$ which reflects the characteristic of the amorphous glass nature. This indicates the absence of long range atomic arrangement and periodicity of the three dimensional network in the quenched material [16-18].

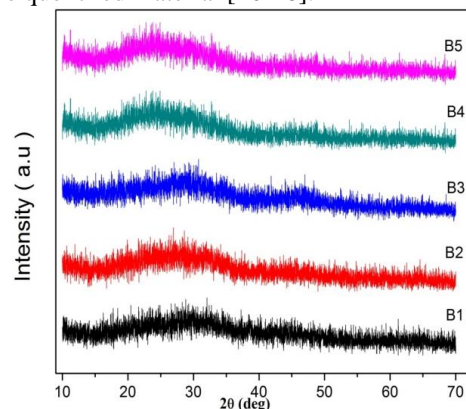


Figure 1: XRD pattern of $\text{Pr}_6\text{O}_{11}-\text{Ag}_2\text{O}-\text{B}_2\text{O}_3$ glass system.

Differential Scanning Calorimetry

The glass transition temperatures (T_g) determined from the Differential Thermal Analysis (DTA) trace of each sample, are summarized in Table 1 and typical DTA trace of glass samples is shown in Figure 2. Variation of glass transition temperatures versus Pr_6O_{11} mol% is shown in Figure 3. These transitions are relatively weak as compared to the conventional transitions reported so far [18]. Therefore reported glasses may be called “soft glasses”. There is a continuous increase in the value of T_g with increasing Pr_6O_{11} concentration in the glass except for the sample with $x=2$. The decrease in T_g can be attributed to the glass forming behavior of Pr_6O_{11} [19]. Pr_6O_{11} enters in the glass matrix causing new species to be formed due to change in oxygen packing density. This process makes the structure relatively strongly packed thereby increasing the value of T_g .

Table 1: Composition mole fractions of glass samples and glass transition measurement.

Sample ID	Nominal composition of samples in mol%			T_g (°C)
	Pr_6O_{11}	Ag_2O	B_2O_3	
B1	0	25	75	417.67
B2	1	24	75	459.15
B3	2	23	75	294.15
B4	3	22	75	446.81
B5	4	21	75	523.31

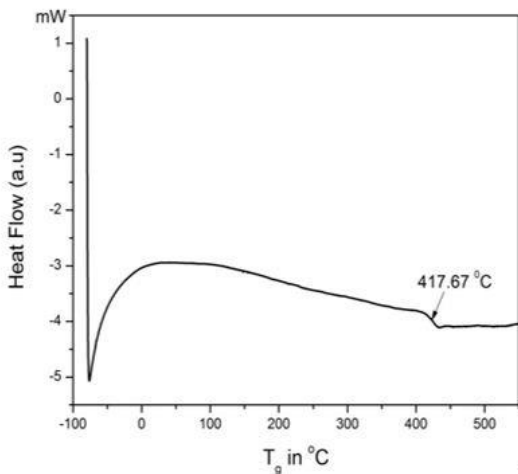


Figure 2: Typical DTA trace of Pr_6O_{11} - Ag_2O - B_2O_3 glass system.

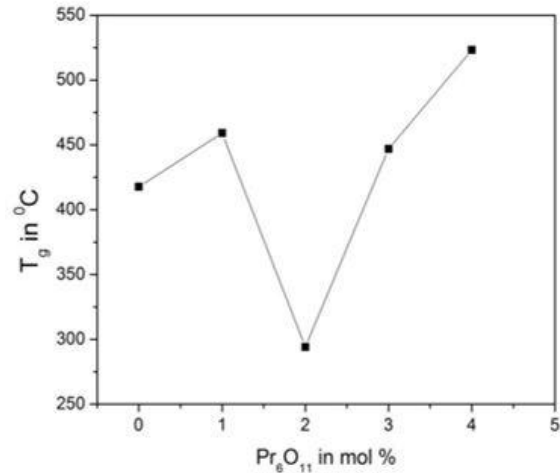


Figure 3: Variation T_g versus Pr_6O_{11} mol% of the glass system.

^{11}B MAS-NMR

^{11}B MAS-NMR spectra of all the glass samples are shown in Figure 4. The spectra reveal the presence of sharp resonance peak at around 18 parts per million (ppm) (with respect to resonance signal of trimethyl boron), which arises from B_4 (boron atom in four co-ordination) [20-23]. There is a split peak at the base of all the signals from B_4 , which arises from three coordinated boron atoms [24]. Thus all the spectra have the appearance of B_4 resonance peak with wings at the base as is expected in glasses containing boron atom in two co-ordinations. The area under the composite spectrum has been apportioned to B_4 and B_3 with a smooth line. A well established feature of borate glass is that their modification by addition of modifying oxides, first leads to conversion of B_4 and B_3 units till the proportions of B_4 and B_3 are equal. Formation of B_4 units is assumed to be occurring initially through the formation of oxygen bridges between $[BO_{3/2}]^0$ units in B_2O_3 .

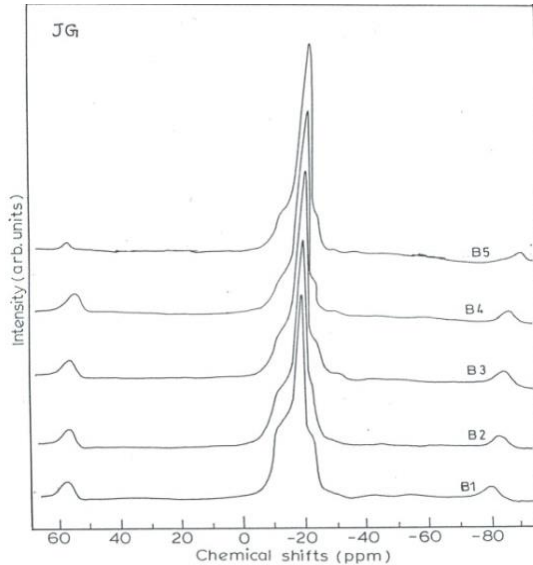


Figure 4: ^{11}B MAS-NMR spectra of glass system

Conclusions

The praseodymium oxide doped silver borate glasses have been synthesized by melt quenching technique. The glasses synthesized were characterized by X-ray diffraction, which did not show sharp peaks confirming the samples prepared are amorphous. All the glasses exhibited characteristic glass transition temperature. The variation of T_g has been examined in light of borate network groups. The thermal properties indicate a strengthening of the glass structure as Pr ions are introduced. ^{11}B MAS-NMR studies on $\text{Pr}_6\text{O}_{11}\text{-Ag}_2\text{O-B}_2\text{O}_3$ glass system have been carried out to ascertain the role of Pr ions in these glasses. ^{11}B MAS-NMR results that the boron ions exist as BO_3 and BO_4 groups. Increasing the Pr_6O_{11} content causes partial conversion of the boron ions from trigonal coordination to tetrahedral coordination.

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