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PHYSICAL PROPERTIES OF BOROTELLURITE GLASS DOPED WITH MANGANESE

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ABSTRACT

Systematic series of borotellurite glasses doped with manganese (100-x) $[(B_2O_3)_{30}(TeO_2)_{70}]$ - xMnO with x = 0.1, 0.2, 0.3 and 0.4 were successfully synthesized by using the melt quenching technique. In this study, the remelting effect of the glass samples on their microstructure were investigated through the density measurement and FT-IR spectra, as well as being evaluated with the XRD techniques. Initial experimental results from XRD measurement show that there were two separate phases probably due to the existing of peak before the sample was remelted. The different physical behaviors of the studied glasses were closely related with the concentration of manganese in each phase. The transition temperatures of these types of glasses were found to decrease with addition of the manganese content and most probably due to the increasing of non-bridging oxygen (NBO) in the borotellurite network.

Keywords: borotellurite glass; density; transition temperature;

INTRODUCTION

Tellurium oxide based glasses are well known because of their special characteristics like high density, high refractive index and good transparency in the far infrared region. Furthermore these glasses are highly stable against devitrification, non-toxic and are resistant to moisture for long periods as compared with those of conventional glasses [1]. It is generally recognized that the refractive index, n, and density, ρ, of many common glasses can be varied by changing the base glass composition [2].

In the present work, borotellurite glasses doped with manganese oxide that consist of MnO with TeO_2 and B_2O_3 as glass formers were successfully prepared by melt quench technique. The main objective of this present work is to determine the optimum percentage concentration of manganese needed by identifying the amorphous nature using X-ray diffraction technique which stabilizes borotellurite glass and form fully amorphous. The term on original sample in this paper represent the first series of borotellurite glasses doped with manganese (100-x) $[(B_2O_3)_{30}(TeO_2)_{70}]$ - xMnO with x = 0.1, 0.2, 0.3 and 0.4. On the other hand, remelted sample represents the sample after the original sample being remelted.

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EXPERIMENTAL

The 13g batch of (100-x) $[(B_2O_3)_{30}(TeO_2)_{70}]$ – xMnO glass system with x = 0.1, 0.2, 0.3 and 0.4 were prepared by mixing all together. The mixture was mechanically grind using agite mortar for homogeneities for 15 minutes. The mixture was then preheated inside an alumina crucible in electrical furnace for half an hour at temperature of 400^{o}C. The preheated mixture was then transferred to the second furnace for one hour at temperature of 950^{o}C. The crucible was constantly shaking inside the furnace for every 15 minutes for homogeneity. The melt then poured into stainless steel cylindrical shape split mould which preheated at 350^{o}C. This immediately transferred to an annealing furnace for two hours at 350^{o}C. After two hours, the furnace was let to cool down at room temperature.

The cylindrical shape of glass samples were then cut using low concentrations diamond blade to obtain a parallel fine surface at 6mm thickness. The unused part of the glass was taken and grind into fine powder. The fine powders then remelt and all the process above repeated to study the remelting effect. The amorphous nature of the glasses was ascertained from XRD analysis using X-ray Diffractometer (PANalytical (Philips) X'Pert Pro PW 3040/60).

The density of each glass (ρ_s) was measured using Archimedes method and distilled water as the immersion liquid. A bulk glass was weighed in air (W_{air}) and immersed in distilled water and reweighed (W_{dw}) where density of distilled water is 1.00gcm^{-3}. The relative density is give such as following relation [3]:

$$\rho_s = \rho_{dw} (W_{air} / W_{dw}) \quad (1)$$

RESULTS AND DISCUSSION

The XRD patterns for several compositions of (100-x) $[(B_2O_3)_{30}(TeO_2)_{70}]$ - xMnO glasses obtained are shown in Figure 1(a) and 1(b). These figures show the occurrence of peak for MnO concentrations for 0.1 and 0.2 mol %. This peak is due to the existence of crystalline phase in the samples, where MnO has disturbed the system of borotellurite glass and formed nucleus. Crystal growth can occur at any temperature below melting temperature, T_m as long as nucleus is available, and nucleus need not have to form during cooling, detectable growth rate can occur at any temperature below T_m [4]. The peak was found to be manganese telluride borate, $Mn_3B_7O_{12.65}Te_{0.85}$. However, at 0.3 and 0.4 mol %, the glass changes completely to amorphous due to the optimum concentration of MnO which work as a stabilizer for the glass.

All these glasses were then remelted in order to study the remelting effect to the structure. The overall features of XRD pattern confirm the amorphous nature for all of these remelted samples (Figure 1b). The characteristic of amorphous structure shows

broad hump at around 2θ= 20 – 30. No peak observed corresponding to MnO indicating that MnO completely entered in the glass matrix. The reconstruction of the glass structure due to the remelt effect avoids the nucleation process for the occurrence of the crystal seed.

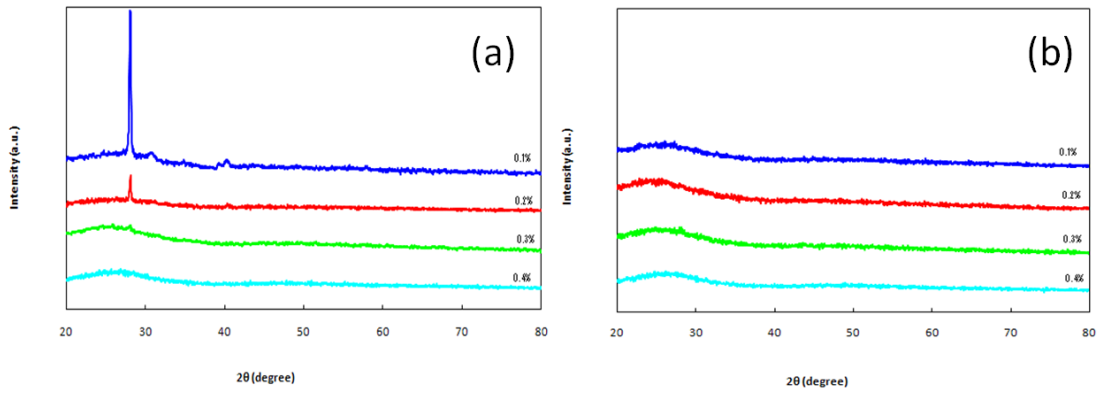

Figure 1. The XRD patterns for MnO–B2O3–TeO2 glasses (a) original sample, and (b) remelted sample

The glasses prepared were free from bubbles and purple in colour. The density, ρ, and molar volume, V_m, for the glass samples are shown in Figure 3. Density of pure borotellurite was increase gradually with the increasing of boron oxide in the glass structure (Figure 3a). However, addition of MnO as a dopant has changed the properties of the glass. These properties changed linearly as a function of glass composition. It can be observed that, density decreases gradually with the compositions for both glasses before and after remelt (Figure 3b-c).

The density results show that as the manganese cation concentration increases the glass structure becomes more open, allowing for the probable formation of increasing number of non-bridging oxygen (NBO) [5]. Also, from Figure 3b and 3c it is found that the molar volume increases with increasing manganese content. In the present samples, the densities vary from 4.57 to 5.56 g cm^{-3} and 3.23 to 4.38 gcm^{-3} after remelted, revealing a linear relationship with obvious systematic trend as a function of manganese content. However, there are slightly different in density between original and remelted samples. This difference is due to the existence of crystal growth inside the glass system. Occurrence of crystal growth causes the decreasing of non-bridging oxygen. Remelting effect of this glass network reconstruct the structure of the glass system and increase non-bridging oxygen inside it causing the density lesser than before it was remelt.

Here, the composition dependence of molar volume gives information about the coordination state of the manganese cations. The density and molar volume for these glasses are consistent with the ionic size, atomic weight, and amount of different elements in the glasses.

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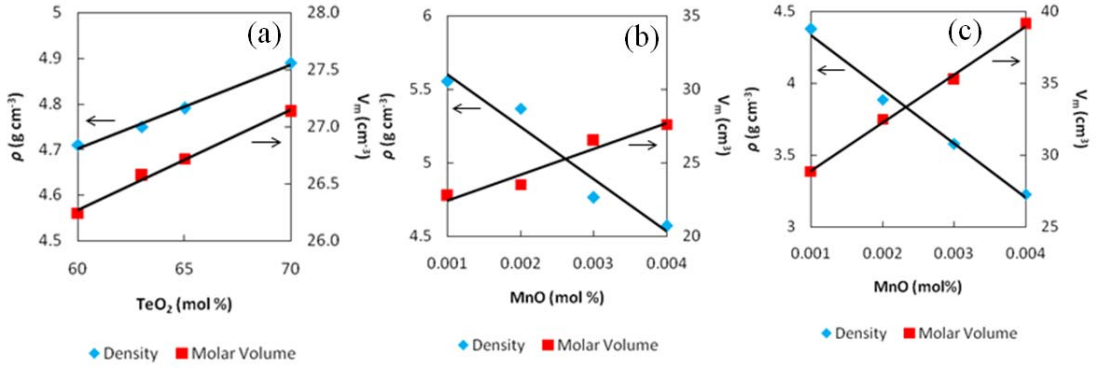

Figure 3:Density and molar volume comparison of (a) borotellurite glasses, (b) original sample and (c) remelted sample

The experimental FT-IR spectra for the borotellurite glasses doped with manganese (100-x) $[(B_2O_3)_{30}(TeO_2)_{70}]$ - xMnO with x = 0.1, 0.2, 0.3 and 0.4 are presented in Figure 4a and 4b. The FT-IR spectral bands of the glasses investigated in this paper and their assignments are summarized in Table 1. This data have been analyzed on the basis of the method given by Condrate [6] and Tarte [7] by comparing the experimental data of glasses with those of related crystalline compounds.

It was found that the quantitative evolution of these glass structures is influenced by the MnO concentration. The MnO addition in the glass matrix composition leads to a drastic decrease in intensity between ~520 and ~650 absorption bands due to Te-O bond $[TeO_4]$ trigonal bypiramidal unit with bridging oxigen and also conribute specific vibration of Mn-O bond [8,9]. If we take into account about the Mn-O bond vibrations contribution to the ~520, it seems that the controlled addition of manganese ions constricts, in a large proportion, the bending motion of different boron-oxygen bonds and gradually increases the number of Mn-O linkages.

Where as, at infrared region 400-1400 cm^{-1}, the vibrations of the B-O arrangements are active [10]. The medium absorption placed at ~1200 cm^{-1} is due to the B-O asymmetric stretching of tetrahedral BO4 [10] and otho-borate group [11, 12]. The intensity of this band is decreasing for original samples from x= 0.1% to x= 0.4%. As for the remelted sample, the intensities of these bands remain the same, as the concentration of manganese ions increase except at x= 0.3%, this may attribute to the occurrence of impurities of crystal structure from manganese telluride borate inside the glass powder during the sample preparation.

The band at intensity ~1400 is due to assymetric of B-O bond from $[BO_3]$ stretching trigonal unit in varied borate rings [8, 12, 13]. The band intensity decreasing as inreasing of concentration of manganese ions for original samples. As for the band at intensity between ~1600 and ~3200, both assign to bending of O-H and assymetric stretching of O-H respectively [14, 15]. Occurance of O-H bond inside this glass is for x= 0.1% to x= 0.3% inside the original samples is correspond to the existance of crytal

structure of manganese telluride borate which is very soluble and easily react with H_2O. As the band intensity at ~1200 and ~1400 decrease, the band intensity at ~1600 and ~3200 also decrease and finally disappear at x= 0.4% for original sample. For the remelted sample, there are no bending of O-H as well as stretching of O-H except at x= 0.3% which attribute to the occurrence of impurities during sample powder preparation.

Table 1: Frequencies and their assignments for FT-IR spectra of (100-x) $[(B_2O_3)_{30}(TeO_2)_{70}]$ – xMnO

Peak positions (cm^{-1})	Assignments
~520	correspond to Mn-O bond
~650	due to Te-O bond [TeO4] trigonal bypiramidal unit with NBO and also conribute specificvibration of Mn-O bond.
~1200	due to assymetric stretching vibration of B-O bond for tetrahedral and ortho-borate group.
~1400	due assymetric of B-O bond from $[BO_3]$ stretching trigonal unit in varied borate rings.
~1600	due to the bending of O-H.
~3200	due to assymetric stretching of O-H.

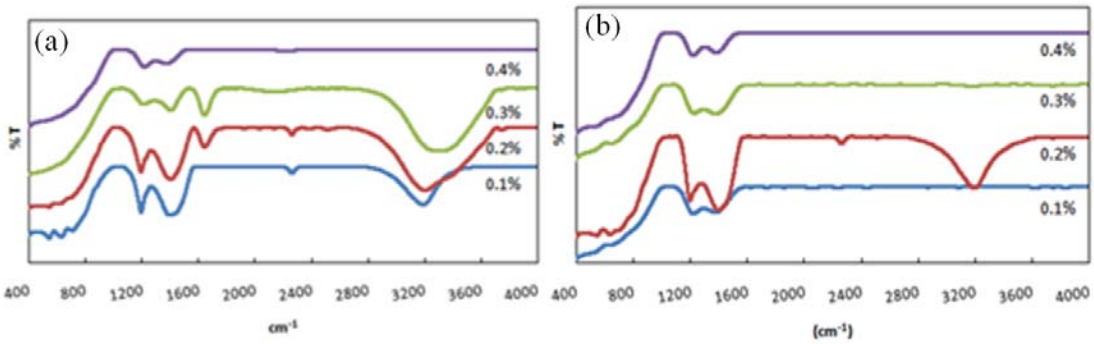

Figure 4: FT-IR spectra of (a) original sample (b) remelted sample

CONCLUSION

Borotellurite glass doped with manganese oxide has been successfully prepared by melt quenching technique. The XRD, density and molar volume of these glasses were reported. The overall features of XRD curve shows that the occurrence of peak for 1 mol % and 2 mol % due to the existence of crystal seed inside the samples, however, for concentration at 3 mol %, the XRD pattern confirm the amorphous nature of this glass. Remelting effect on the other hand reconstructs the glass structure and avoids nucleation for the crystal growth. The density was observed to decrease with increasing of MnO for this original and remelted glass samples. However, slight different in

density was shown for both glass systems due to the existence of crystal growth inside the remelted glass network. This effect reconstruct structure of the glass system and increase non-bridging oxygen inside it causing the density lesser than before it was remelt which have been shown by FT-IR spectra analysis.

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