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Compositional dependence thermal and optical properties of a novel germanate glass

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ABSTRACT

A series of zinc lithium germanate glasses of the composition $(45-x)Li_2O$–$xZnO$–$55GeO_2$ have been synthesized via melt quenching technique. Dependencies of their thermal and optical properties on composition were investigated. It is found that the gradual replacement of Li_2O by ZnO, decreases the glass transition temperature from 430 to 280 °C and increases the thermal stability (ΔT) of the studied glasses. The optical band gap E_{opt} also decreases from 2.31 to 1.40 eV with increasing the mole content of ZnO.

1. Introduction

The increased indigence and miscellaneous applications of modern electronic devices have resulted in competition for cost, reliability and speed. This in turn has led to the search for new materials which can meet the specific requirements. Germanate glasses are among these materials and have a number of technological applications, such as telecommunications, optics industries, optical fibers and infrared-transmitting windows. The outer electronic structure of germanium is the same as for silicon, but its atomic radius is greater. This suggests a weaker bonding between germanium and oxygen, which leads to better infrared transmission than silicon. The better infrared transmission is what makes germanates so attractive [1–5].

The change of glass composition affect the induced optical absorption due to several reasons, namely the polarization power of network formers, modifiers, their coordination numbers, the concentration of non-bridging oxygen, the presence of multivalent network forming and modifying ions [6].

Thermal and optical properties are attributed to inner structure of materials. Thus, it is of prime importance to establish relationship between structure and properties and to know how zinc oxide influences thermal and optical properties of glasses.

In this work, we prepared a novel zinc lithium germanate glass system and studied the effect of zinc oxide addition on the thermal and optical properties of lithium germanate glasses.

2. Experimental details

A series of glass samples with the molar formula $(45-x)Li_2O$–$xZnO$–$55GeO_2$, ($x=0$, 10, 15, 20, and 25 mol%) were prepared. Appropriate amounts of reagent grade Li_2O, ZnO and GeO_2 were well mixed and melted in porcelain crucibles using an electric furnace at a temperature ranging between 1150 °C and 1250 °C for 2 h, depending on the glass composition. The melt was swirled frequently to insure the homogeneity. The melt was then poured and pressed between two stainless steel plates to form disks of 2 mm thickness. The glasses were stored in a desiccator until required.

The density (ρ) was determined at room temperature using the Archimedes method with toluene as an immersing liquid. Four samples of each glass were used to determine the density. The density values were reproducible to ± 0.01 g/cm^3. The molar volume (V_m) was calculated using the formula:

$$V_m = \sum n_i M_i / \rho \quad (1)$$

Here M_i is the molecular mass for component i and n_i is the molar ratio.

A Labsys™ TG-DSC16 SETARM calorimeter was used to determine the transformation temperature (T_g) of the studied glasses,

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Table 1
The compositions, density, molar volume, glass transition temperature, T_g, glass crystallization temperature, T_c and ΔT for $(45-x)Li_2O$–$xZnO$–$55GeO_2$ glasses.

Sample No.	ZnO (mol%)	ρ (g/cm^3)	V_m (cm^3/mole)	T_g (°C)	T_c (°C)	ΔT (°C)
Zn0	0	3.48	20.39	430	612	182
Zn10	10	3.66	20.80	370	570	200
Zn15	15	3.73	21.10	320	580	260
Zn20	20	3.80	21.39	290	608	318
Zn25	25	3.91	21.44	280	610	330

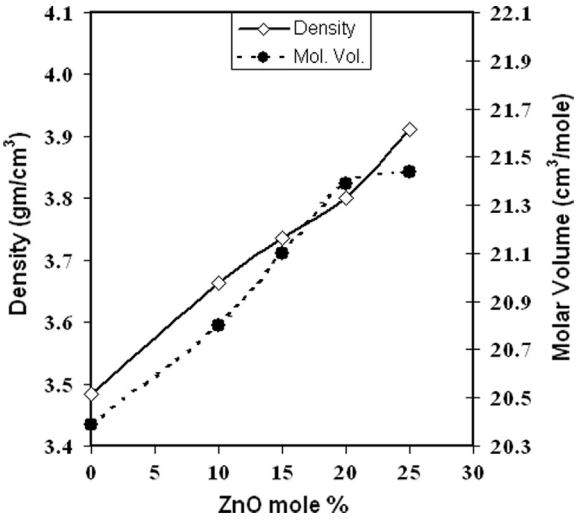

Fig. 1. The dependence of density, ρ (g/cm^3) and molar volume, V (cm^3/mole) for: $(45-x)Li_2O$–$xZnO$–$55GeO_2$ glasses, on composition where, x is as indicated (all lines are drawn as guides to the eyes).

Table 1. A 20 mg sample was placed in an Al_2O_3-crucible. The latter was heated under argon from room temperature up to 800 °C, at a rate of 10 °C/min. The error limit in the T_g values is estimated as ± 5 °C.

Optical absorption spectra of prepared glasses were recorded at room temperature, by using a Jasco V-530 UV/Vis spectrophotometer in the wavelength region 190–1000 nm with a resolution of 2 nm.

3. Results and discussion

3.1. Density and molar volume

The importance of the density for describing the structure of a glass is evident [7]. Fig. 1 shows the dependence of the density and molar volume of prepared samples of the glass system: $(45-x)Li_2O$–$xZnO$–$55GeO_2$, where $x=0$, 10, 15, 20, and 25 mol%, ZnO content. As expected the addition of ZnO to the glass network causes some type of structural rearrangement of the atoms. This figure indicates that the glass density is increased from 3.48 to 3.91 g/cm^3 as the mol% of ZnO content is gradually increased from 0 to 25 mol% and the molar volume increased from 20.39 to 21.44 cm^3/mole in the same compositional region.

The observed increase of the density with the gradual increase of ZnO mole content from 0 to 25 mol% is due to the heavier zinc oxide molecular weight (81.408 g/mole) compared with the lithium oxide molecular weight (29.877 g/mole) in the glass samples. Increases in the density of the glass sample also result in changes in the crosslink density. The increases in the density of the glass samples are attributed to the formation of new linkages in the glass structure. The Zn^{2+} ion tends to occupy interstitial sites within the highly open glass network. As reported earlier, the structure of lithium germanate glass network consists of the following structural units: GeO_4 and GeO_6 [8–10]. The increase in the density is due to glass structural changes caused by the influence of Zn^{2+} in breaking the Ge–O networks. All oxygen atoms from ZnO are used to rupture the Ge–O–Ge bridges, which is accompanied by the transformation of nearly all participating GeO_6 groups into GeO_4 groups [11]. The increase in the molar volume, V_m indicates an increase in the inter-atomic distance, and ZnO acts as a modifier. In this case, the non-bridging oxygens (NBOs) are increased in number in the lithium germanate network; therefore, V_m increases. Therefore, the compactness of the glass sample will decrease.

3.2. Thermal analysis

Fig. 2 shows the compositional dependence of the DSC curves including the characteristic temperatures (T_g, T_c) for the studied glasses recorded at a heating rate 10 °C/min. It is clear that, the whole glasses exhibit a single endothermic peak attributed to the glass transition temperature range which represents the strength or rigidity of the glass structure. At higher temperatures, there is a single exothermic peak attributed to the full crystal growth. The appearance of a single peak due to the glass transition temperature in DSC pattern indicates the high homogeneity of the studied glasses [12].

From inspection of Fig.2 and Table 1, it is found that, the nature of the glass in the vicinity of the glass transition is very sensitive to its composition, where the glass transition temperature, T_g decreases with gradual increase of ZnO mole content.

It is known that DSC investigations of the glass transition temperature are useful in suggesting structural changes that take place by composition changes. This is because T_g is very sensitive to any change of the coordination number of the network-forming atoms and also to the formation of non-bridging oxygen [13–16]. The decrease of T_g with composition up to 25 mol% of ZnO implies a decrease in the rigidity of the glass network [16]. The observed decrease in T_g up to 25 mol% of ZnO of the present investigated glass system could be ascribed to some structural changes such as transformation of some GeO_6 groups into GeO_4 groups leading to

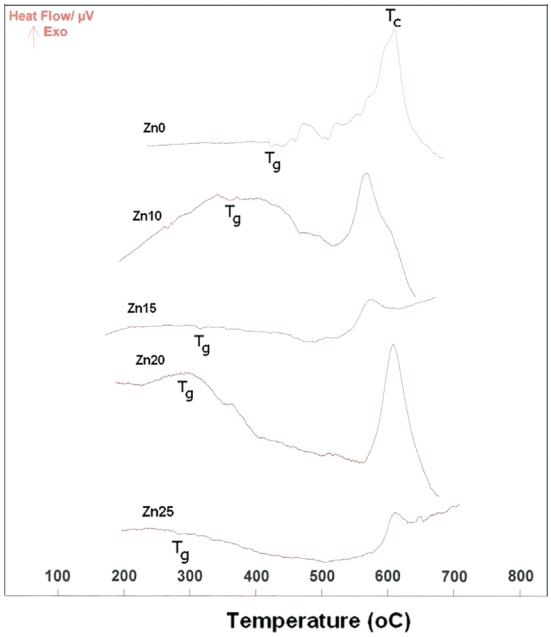

Fig. 2. Typical DSC traces with the characteristic temperatures (T_g and T_c) for $(45-x)Li_2O$–$xZnO$–$55GeO_2$ ($x=0$, 10, 15, 20, and 25 mol%) glasses recorded at heating rate 10 °C/min.