Structural, optical and thermal characteristics of GeO$_2$-PbO-SrO-AlF$_3$-MgF$_2$ glasses

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1. Introduction

The middle infrared range, at the wavelength range of 3–5 µm, is the most important atmospheric transmission window, and transparent materials in this range are especially important for optical applications [1]. It is well known that transparent materials for optical applications must be isotropic, easily fabricated at low costs and provide maximum transmission. However, one ideal window satisfying all the requirements does not exist and selection of an infrared window is often based on compromises instead of choices [2–4].

Among window materials for IR applications (e.g. ZnS, sapphire, AlON and some glasses), the heavy metal oxide glasses are technologically important due to their potential use as low loss optical glasses in the visible-to-infrared region [2–4]. Germanate glasses are of particular interest because of their infrared transmission, higher glass-forming ability and good chemical durability. These glasses are good candidate for infrared windows operating in the 0.5–5 µm region [1]. Furthermore, due to stronger inter-ionic force between Ge$^{4+}$ and O$^{2-}$, these glasses manifest better thermal stability and are mechanically stronger than other IR transmitting glasses [1]. However, this compound has some disadvantages, such as high melting temperature and high viscosity.

The germinate glasses usually contain high concentration of hydroxyl groups, which cause a strong absorption band around 2.75–2.90 µm and depress the transmittance in 2.5–5 µm region [5,6]. Several methods including melting in dry atmosphere, melting in vacuum, bubbling dry gases through the melt, addition of bubbling agents and fluoride to the melt, preliminary drying of constituents and diffusion from the solid glass may be used to remove the O-H absorption bands from composition. Among all methods, the addition of bubbling agents (such as carbonates) and substitution of oxide chemical precursors by fluorides are effective methods in moving H. For instance, Jiang [5] and their coworkers reported the replacement of PbO by PbF$_2$ in GeO$_2$-PbO system and found less hydroxyl existed in germanate glasses. Fray and Nielse [6] presented low loss germinate glasses by using carbonates (CaCO$_3$ and Na$_2$CO$_3$) and fluorides (AlF$_3$) replacing PbO component in GeO$_2$-PbO system. The presented results with Feng et al. [7] about the effect of composition and preparation procedures on the content and vibration frequency of hydroxyl groups in Er$^{3+}$-doped GeO$_2$-TeO$_2$-ZnO-NaO-Y$_2$O$_3$ glasses are the other studies in this field.

PbF$_2$ is the best fluoride compound [5] that can be added to germinate glass composition, but this compound has hazardous environmental problems. In this regard, the AlF$_3$ and MgF$_2$ are introduced as alternatives [8]. It is well known that, by addition of fluorides to germanate glasses, the glass network breaks and the viscosity, glass-forming ability and glass transition temperature reduce [6–12]. Based on our previous study [13], the addition of SrO compound by high-bounding strength to fluoride containing germinate glasses can reduce the deleterious effects of fluorides on thermal and optical properties of formed glasses.
In the presented work, the effects of SrO on different characteristics of GeO$_2$-PbO and the effects of AlF$_3$ and MgF$_2$ on GeO$_2$-PbO-SrO glassy systems have been investigated. In this regard, the desired glasses were prepared using conventional melt quenching technique, and the structural and thermal properties of prepared glasses were evaluated. Moreover, the optical characteristics of prepared samples were analyzed and the values of the optical band gap and Urbach energy were established.

2. Experimental

High-purity PbO (99.99% purity, 200 µm), SrCO$_3$ (99.99% purity, 15 µm), AlF$_3$ (99.9% purity, 50 µm) and MgF$_2$ (99.99% purity, 15 µm) were used as raw materials. Different combinations of precursors, based on Table 1, were melted in a zirconia crucible at 1250°C for 60 min. The melts were quenched between two stainless steel plates and finally annealed at 450–500°C for 120 min.

The structure of prepared specimens was monitored using X-ray diffraction (XRD) technique. The diffractometer was Philips PW3710 with Cu Ka radiation at 40 kV. The analysis conditions were: 20 range: 10–60°; step size: 0.05°; time per step 1 s. The microstructure of annealed samples was studied using field emission scanning electron microscopy (VEGA-STEMSCAN-XMU) at an accelerating voltage of 20 kV. The crystallization (Tx) and glass transition (Tg) temperature of prepared glasses were followed by differential thermal analyzer (SDT Q600). The thermal analyses were performed from room temperature to 900°C with a heating rate of 10°C/min. It is important to note that, the differential thermal calorimetry (DSC) curves were too broad to estimate glass transition temperature and the exact Tg values were estimated using the first derivative of DSC curves (DDSC). Optical properties of prepared samples were also measured using a Bruker Tensor 27 Fourier transform infrared (FTIR) spectrometer (in the wavenumber range of 400–1400 cm$^{-1}$) and a Jasco V-530 UV/Vis spectrophotometer (in the wavelength region 190–1000 nm).

Table 1. The chemical compositions of different GeO$_2$-PbO-SrO-MgF$_2$-AlF$_3$ specimens which were investigated in this work.

| S.N. | GeO$_2$ | PbO | SrO | MgF$_2$ | AlF$_3$ |
|------|--------|-----|-----|---------|---------|
| 1    | 50     | 50  | -   | -       | -       |
| 2    | 50     | 40  | 10  | -       | -       |
| 3    | 50     | 30  | 20  | -       | -       |
| 4    | 50     | 30  | 10  | 10      | -       |
| 5    | 50     | 20  | 10  | 20      | -       |
| 6    | 50     | 30  | 10  | -       | 10      |
| 7    | 50     | 20  | 10  | -       | 20      |

3. Results and discussion

There are several factors such as composition, superheat and solidification rate that influence the structure and optical properties of germanate glasses. A slight variation in these parameters can often cause large variations in the microstructure and properties of samples [1–3]. In the present study, all of these parameters were kept nominally constant and the effects of SrO, MgF$_2$ and AlF$_3$ on the microstructure and optical properties of GeO$_2$-PbO glassy system were investigated.

To understand the effects of SrO on different characteristics of GeO$_2$-PbO glasses, three different combinations of initial precursors, based on Table 1, were melted and quenched at same condition. The XRD patterns of 50GeO$_2$-(50-x)PbO-xSrO (x = 0, 10, 20) as-quenched samples are presented in Figure 1. As seen, there is not any evidence of sharp diffraction lines in these XRD patterns. All X-ray diffractograms exhibit broad diffuse scattering halo confirming long-range structural disorder characteristic of the amorphous network in formed glasses. This result indicates that, regardless to the difference in chemical composition, all specimens are in the amorphous state.

The DSC curves of prepared glasses are shown in Figure 2. As seen, these curves only consists of one changing in the slope of the base line and one exothermic peak which reveals to glass transition (Tg) and crystallization (Tx) temperature, respectively. The Tg and Tx of 50GeO$_2$-50PbO are estimated at about 460°C and 810°C, which is in agreement with presented results by Jiang [14] and Dumbaugh [15]. As seen, the Tg and Tx values increase toward 580°C and 831°C by increasing the SrO content up to 20 mol %. Furthermore, the ΔT (=Tx−Tg) of 50GeO$_2$-(50-x)PbO-xSrO (x = 0, 10, 20) glasses is more than 200°C.

It is well known that Tg mainly depends on two main factors as follows [8,9]:

1. The network connectivity: The topological model can be used for depiction of glass network in covalence glasses. This model argues that the glass structure is predominately controlled by the Mean Coordination Number (MCN) [10,11]:

$$MCN = \sum x_iMCN_i = (\sum MCN)\textit{cations} + (\sum MCN)\textit{anions}$$  \hspace{1cm} (1)

where $x_i$ is the abundance of the ith component of a glass and MCN$_i$ is the valency of the ith constituent atoms. Based on this model, the MCN value of pure GeO$_2$ in amorphous state is MCN = 4. By addition of 50 mol % of lead oxide to glass composition, the MCN value decreases to about 3. This point illustrates that the Ge-O-Ge connectivity in glass network has
been destroyed and some of GeO₄ tetrahedral units convert to GeO₆ octahedral ones. In other words, the density of non-bridging oxygens increases and the glass network becomes more fragile. In fact, the SrO has the same effect on glass network of germanate glasses and with the substitution of SrO with PbO (with same valance), the MCN value as well as network connectivity remain unchanged. So, this parameter is not useful to explain the change in glass transition temperature.

2. The strength of the chemical bond between the components: According to Gorlich [12], glass transition temperature can increase with increasing the strength of the chemical bond between the components. By attention to this point, replacement of weak Pb-O bonds with rigid Sr-O is the main reason of increasing the thermal stability of GeO₂-PbO-SrO with increasing the SrO content.

The UV-Vis and FTIR transmission spectra of 50GeO₂-(50-x)PbO-xSrO (x = 0, 10, 20) glasses are shown in Figure 3. As seen, the similar spectra were obtained for glass specimens with different compositions. There is no sharp absorption edge in UV-Vis spectra which confirms the glassy state of formed specimens [16,17]. Moreover, there is one absorption peak at 2.85 µm in FTIR spectra which can be related to the presence of hydroxyl group impurity [5,6].

Based on UV-Vis spectra, two important optical parameters can be calculated as follows:

1. The optical band gap energy: For amorphous materials, the absorption coefficient exhibits a sharp
increase just before the band gap. The relation between absorption coefficient and the incident photon energy is given by Davis and Mott \[27\] relation:

\[
a = \beta (\frac{\hbar \nu - E_{\text{g}}^{\text{opt}}}{\hbar \nu})^n
\]

where \(\beta\) is a constant related to the extent of the band tailing, \(n\) is the index which can have different values 2, 3, 1/2 and 1/3 corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. Therefore, by plot \((a\hbar \nu)^{1/n}\) vs. photon energy (Tauc’s plots), the intercept of the obtained line divided by slope is equal to the energy band gap of optical transitions.

2. The Urbach energy: The optical absorption in amorphous semiconductors near the absorption edge is usually characterized by three types of optical transitions corresponding to the transitions between tail and tail states, tail and extended states, and extended and extended states. The first two types correspond to \(\hbar \nu \leq E_{\text{g}}^{\text{opt}}\) and the third one corresponds to \(\hbar \nu \geq E_{\text{g}}^{\text{opt}}\). Thus, the plot of absorption coefficient versus photon energy \((\alpha \hbar \nu)\) has three different regions. In the second region, the absorptions is related to transitions from the localized tail states above the valence band edge to extended states in the conduction band and/or from extended states in the valence band to localized tail states below the conduction band. The spectral dependence of absorption coefficient usually follows the so-called Urbach rule:

\[
\alpha = \beta \exp\left(\frac{\hbar \nu}{E_U}\right)
\]

By attention to this equation, and least-square fitting of \(\ln \alpha\) against \(\hbar \nu\) curves in the tailing part of localized states \[17\], the Urbach energy \((E_U)\) can be calculated.

In this regard, the short-wavelength absorption edge, Urbach energy and direct and indirect allowed optical band gaps of 50GeO\(_2\)-(50-x) PbO-xSrO \((x = 0, 10, 20)\) glasses are presented in Table 2. As seen, the \(E_{\text{g}}^{\text{opt}}\) and \(E_U\) values of different samples are in the range of 2.98–3.02 and 0.27–0.28 eV, and the replacement of PbO with SrO in 50GeO\(_2\)-50PbO glass has negligible effect on optical properties of prepared glasses. In fact, the same MCN value and the density of non-bridging oxygen in glass compositions are the main reasons of same optical properties of 50GeO\(_2\)-(50-x) PbO-xSrO \((x = 0, 10, 20)\) glasses.

To investigation of the effect of MgF\(_2\) and AlF\(_3\) on structural, thermal and optical properties of GeO\(_2\)-PbO-SrO glassy systems, the XRD patterns of prepared samples in the presence of MgF\(_2\) and AlF\(_3\) are presented in Figures 4 and 5, respectively. As seen, the X-ray patterns of 50GeO\(_2\)-30PbO-10SrO-10MgF\(_2\) and 50GeO\(_2\)-30PbO-10SrO-10AlF\(_3\) as-quenched specimens exhibit one broad diffuse scattering halo (in \(2\theta\) range of 20–40°) confirming a long-range structural disorder characteristic of the amorphous network in these two samples. In contrast, there are several sharp peaks in the XRD patterns for 50GeO\(_2\)-20PbO-10SrO-20MgF\(_2\) and 50GeO\(_2\)-20PbO-10SrO-20AlF\(_3\) glasses, which indicate that these samples are not fully amorphous. This result is in agreement with presented FESEM micrographs in Figure 6.

Based on DSC curves which are presented in Figure 7, the values of \(T_g\) and \(T_x\) of prepared glasses decrease with the substitution of magnesium and aluminum fluorides with PbO. In fact, fluorine and

![Figure 3](image-url) The (a) UV-Vis and (b) FTIR spectra of 50GeO\(_2\)-(50-x)PbO-xSrO \((x = 0, 10, 20)\) as-quenched samples.

![Table 2](image-url) The cutoff wavelength \((\lambda_0)\), direct and indirect allowed optical band gaps and Urbach energy of different GeO\(_2\)-PbO-SrO-MgF\(_2\)-AlF\(_3\) specimens which were investigated in this work.
oxygen ions have closely similar ionic radii and field strength, but a different valence. By addition of fluorides to composition, some oxygen ions replace by fluorine and bridging oxygens replace by non-bridging fluorine. Moreover, the amount of Ge-F and Pb-F bonds with considerable ionicity in comparison with Ge-O and Pb-O increases in glass structure [12]. In this condition, the glass network breaks and the viscosity, glass-forming ability and glass transition temperature reduce [18–21]. The UV-Vis and FTIR transmission spectra of 50GeO$_2$-(40-x)PbO-10SrO-MgF$_2$ (0, 10, 20) and 50GeO$_2$-(40-x)PbO-10SrO-AlF$_3$ (0, 10, 20) as-quenched samples are presented in Figures 8 and 9, respectively. The values of short-wavelength absorption edge, Urbach energy and direct and indirect allowed optical band gaps of prepared glasses are also presented in Table 2. It is important to note that the S.N. = 5, and S.N. = 7 do not show any transparency and their optical characteristics are missing in Table 2. Based on these
results, the UV-Vis-IR transmittance and other optical characteristics of prepared glasses decrease by increasing the percentage MgF$_2$ and AlF$_3$ in glass composition. This result can also be referred to the decreasing in the number of bridging oxygens, glass network connectivity and atomic bonding strength with increasing the fluoride content.

4. Conclusion

From the investigation of structural, optical and thermal characteristics of GeO$_2$-PbO-SrO-AlF$_3$-MgF$_2$ glasses, the following conclusions can be made:

1. The glass-forming ability and thermal stability of GeO$_2$-PbO glasses increased by replacement of PbO with SrO in glass composition.
2. The replacement of PbO with SrO in 50GeO$_2$-50PbO glass composition had negligible effects on optical properties of prepared samples and the values of $E_{g}^{opt}$ and $E_U$ of GeO$_2$-PbO-SrO glasses were estimated in the range of 2.98–3.02 and 0.27–0.28 eV, respectively.
3. The optical properties, overall transparency, glass-forming ability and thermal stability of GeO$_2$-PbO-SrO glasses have decreased by replacement of PbO with MgF$_2$ and AlF$_3$. 

Figure 7. The DSC curves of (a) 50GeO$_2$-40PbO-10SrO, (b) 50GeO$_2$-30PbO-10SrO-10MgF$_2$ and (c) 50GeO$_2$-30PbO-10SrO-10AlF$_3$ as-quenched samples.

Figure 8. The (a) UV-Vis and (b) FTIR spectra of 50GeO$_2$-(40-x)PbO-10SrO-MgF$_2$ (0, 10, 20) as-quenched samples.

Figure 9. The (a) UV-Vis and (b) FTIR spectra of 50GeO$_2$-(40-x)PbO-10SrO-AlF$_3$ (0, 10, 20) as-quenched samples.
4. The values of $E_{g}^{opt}$ of GeO$_2$-PbO-SrO-MgF$_2$-AlF$_3$ glasses were estimated in the range of 3.2–3.5 eV which was lower than the presented results in GeO$_2$-PbO and GeO$_2$-PbO-SrO systems.

Highlights

1. We study the optical properties of GeO$_2$-PbO-SrO-AlF$_3$ transparent glass-ceramics.
2. We study the effect of AlF$_3$ and MgF$_2$ on optical properties of GeO$_2$-PbO-SrO glasses.
3. We study the thermal behavior of GeO$_2$-PbO-SrO-AlF$_3$-MgF$_2$ glass.

Disclosure statement

No potential conflict of interest was reported by the authors.

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