Finite Element Simulation of Pyroplastic Deformation, Anisotropic Shrinkage and Heterogeneous Densification for Ceramic Materials During Liquid Phase Sintering Process

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ABSTRACT

Pyroplastic deformation is a distortion of the ceramic shape during the sintering process. It occurs because of the flow of the vitreous phase at high temperature and the applied stress due to the weight of the product during the sintering process. The aim of this paper is to describe a numerical-experimental method to evaluate the pyroplastic deformation, to predict the anisotropic shrinkage and heterogeneous densification for ceramic materials during the liquid phase sintering process, as a function of the sintering time. For this purpose, three experimental configurations including midpoint deflection, sinter bending, and free sintering test were designed. The finite element method is implemented by the CREEP user subroutine code in ABAQUS. The fair accordance between simulation results and experimental data reveals that the shear and bulk viscosity modulus as well as dynamic viscosity used in the simulation are near the real ones. The anisotropic shrinkage factor K_{xy} has been proposed to investigate the shrinkage anisotropy. It has been shown that the shrinkage along the normal axis of casting slip is about 1.5 times larger than that of casting direction. The inhomogeneity in Von-Misses, pressure, and principal stress intensifies the density non-uniformity in the samples.

1-Introduction

Among window materials for infrared (IR) applications, the glasses based on germanium oxide (germanate glasses) have been of interest due to the excellent combination of chemical durability, availability in desired shape and size [1-7], IR transparency, high non-linear reflection index, high infrared absorption coefficient, high coefficient of thermal expansion, high density, and low glass transition temperature.

Based on the literature, germanate glasses exhibit an anomalous behavior versus composition. For instance, density, refractive index, electrical conductivity, viscosity, and chemical stability of alkali-containing germanate glasses go through a maximum or minimum at 10-20 mole % of alkali oxide [1-7]. It is well known that these anomalous behaviors are in direct relation with the structural units of

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glassy network [8, 9]. The change in the coordination state of germanium with oxygen followed by conversion of GeO6-octahedra to GeO4-tetrahedra is an important reason for describing these behaviors [1, 5-8].

Although based on structural modeling, it is suggested that the anomalous behavior can also appear in the PbO-GeO2 glass system [6-13], there is not any report about this behavior in this glassy system [4-8]. Moreover, the exact effect of PbO on structural and optical properties of PbO-GeO2 glasses has not been properly investigated. So, the present work was motivated by a need to shed additional light on the structural and optical characterizations of PbO-GeO2 glasses. In fact, the anomalous behavior in optical properties of PbO-GeO2 glasses is the main novelty of this work.

2- Experimental

High purity GeO2 (99.9% purity) and PbO (99.99% purity) were used as the raw materials. Different mixtures of GeO2-PbO (based on Table 1) were melted in an alumina crucible at the temperature range of 1350oC for 30 min and 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. In the present experiments, yellowish transparent glasses, without neither bubbles nor inclusions, were easily formed on rapid quenching of the melts.

The structure of prepared specimens was monitored using XRD. The diffractometer was Philips PW3710 with Cu-Ka radiation at 40 kV. The analysis conditions were: 2θ range: 10-100o; step size: 0.05o; time per step 1 s. Structural characterizations of the as-quenched samples were carried out by scanning electron microscopy (VEGA-TESCAN-XMU). Optical properties of the prepared samples were also measured using a Bruker Tensor 27 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).

3-Results and discussion

In order to understand the effects of initial composition on microstructural and optical properties of GeO2-PbO glasses, six different combinations of initial precursors, based on Table 1, were melted and quenched under the same conditions and the prepared samples were examined using XRD, SEM, FTIR and UV-Vis

techniques. The XRD patterns of three selected samples (S.N=1, S.N.=3 and S.N.=6) are presented in Fig. 1. These X-ray diffractograms highlight the amorphous nature of all studied samples.

Table 1. The chemical compositions of different GeO2-PbO specimens investigated in this work.

S.N.	Chemical Composition (mole %)	
	GeO2	PbO
1	85	15
2	80	20
3	75	25
4	70	30
5	65	35
6	55	45

The X-ray patterns exhibit a broad diffuse scattering at low angles, confirming a long-range structural disorder characteristic of the amorphous network. This result is in agreement with Imaoka's [15] study which reported that the glass-forming region of GeO2-PbO system is extended to 57 mole % PbO. Of course, the SEM results (Fig. 2) showed that the structures of the formed glasses are not completely uniform and there is an evidence for glass phase segregation (as small isolated amorphous phase which is virtually undetectable by XRD) in the matrix.

The absorption spectra of GeO2-PbO glasses in the ultra-violet and visible range are shown in Fig. 3. As can be seen, similar spectra were obtained for glass specimens with different compositions. In fact, there is no sharp absorption edge in these absorption spectra. The absorption edge in the case of crystalline materials is very sharp, whereas in the amorphous ones it has a finite slope. In this regard, the absorption spectra of GeO2-PbO glasses also confirm the glassy state of the formed specimens [16].

Variation of the absorption band edge wavelength (cut off wavelength), λ0, as a function of PbO content is shown in Fig. 4 and tabulated in Table 2. As can be seen, the cut off wavelength has a minimum at 25% mole of PbO. On the other hand, λ0 slightly shifts toward shorter wavelengths from 361 to 348 nm (higher energies) as the PbO mole% increases to 25% and then gradually shifts from 348 to 394 nm (lower energies) as PbO mole %

increases from 25 to 45. To explain this anomaly, the FTIR spectra of the prepared glasses are presented in Fig. 5. According to this figure:

1- The FTIR spectra of different glassy samples show broad absorption bands. This point is in agreement with the amorphous nature of the specimens as suggested by X-ray diffraction patterns.
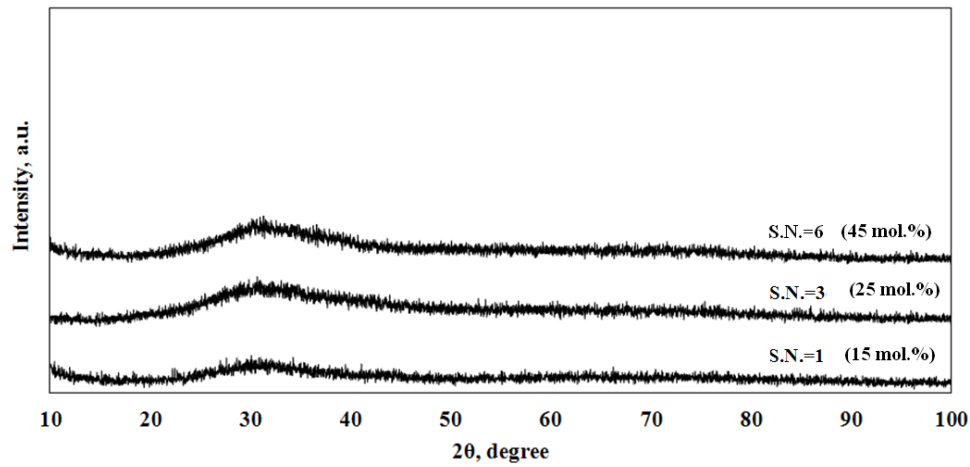

Fig.1. XRD patterns of GeO2-PbO glasses with different percentages of PbO.
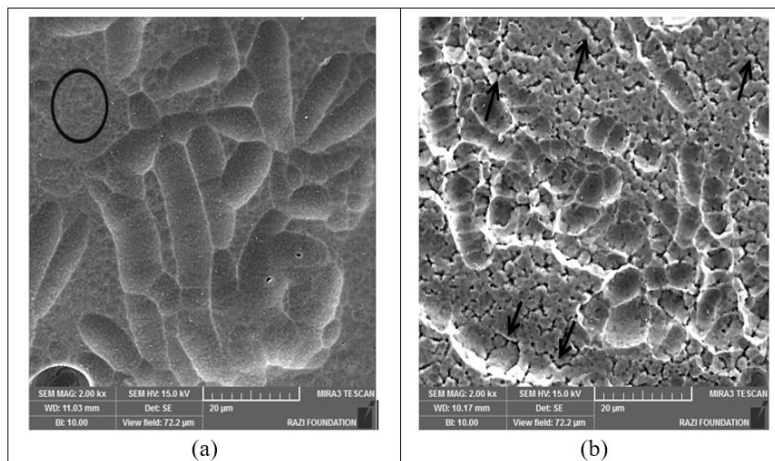

Fig. 2. SEM microphages GeO2-PbO glasses after the quenching process; a) S.N.=1 and b) S.N.=3
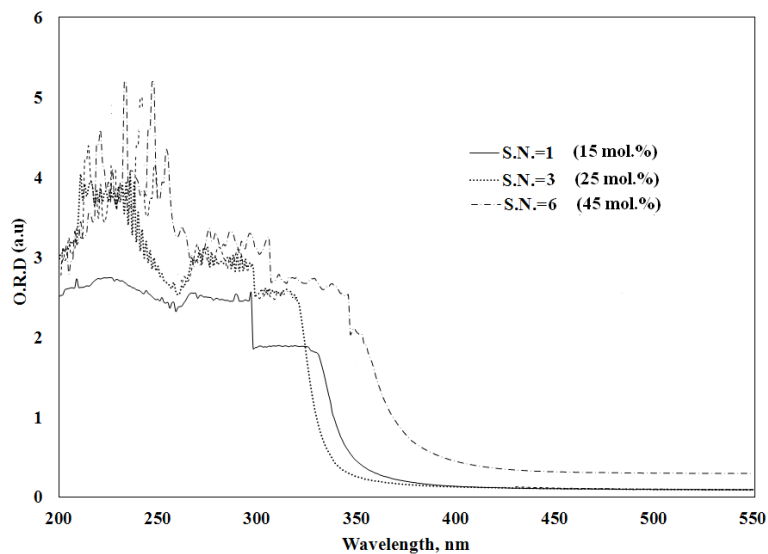

Fig. 3. Variation of optical radiation density with wavelength of S.N.=1, S.N.=3 and S.N.=6
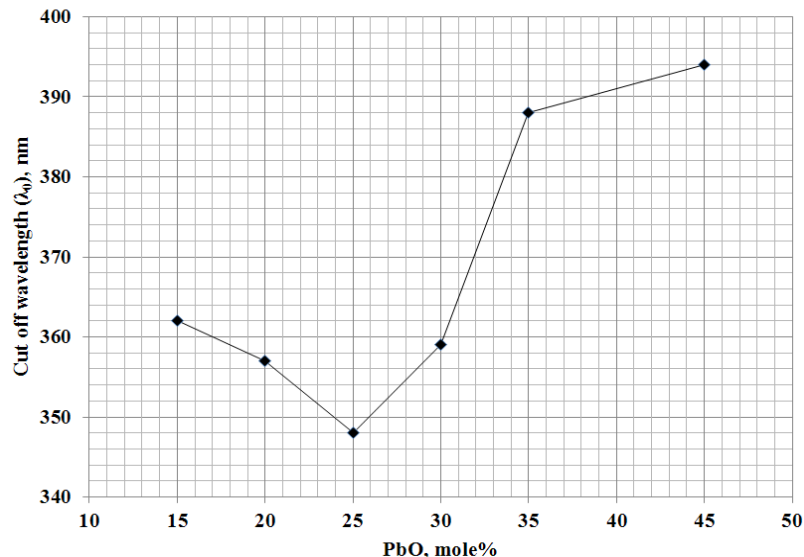
Fig. 4. Variation of the absorption edge λ0, as a function of PbO in GeO2-PbO glasses

2- The infrared absorption spectra of all glassy specimens are similar, indicating that all prepared glasses have a similar structural unit. These absorption spectra are characterized by two wide absorption bands around 500-700 and 700-1100 cm^{-1}. The absorption at 580 cm^{-1} indicates bending and symmetric stretching vibration of the Ge-O-Ge of GeO4 tetrahedral unit (with the Ge-O bonds of 1.739±0.002 Ao) [14]. The band at 700-1100 cm^{-1} wavenumbers can be divided to three peaks at 715, 875 and 1020 cm^{-1}. The first peak is related to the stretching vibration mode of the Ge-O-Ge bond in GeO6 octahedral units of germanium oxide (where four Ge-O bonds are of 1.827 Ao, while the other two are of 1.902 Ao [14]), the second is related to anti-symmetric stretching vibration mode of the Ge-O-Ge bond in GeO4 tetrahedral units [18], and the third is related to anti-symmetric bending vibration of the Pb-O-Pb bond in [PbOn] units. Based on these FTIR spectra (Fig. 5), the Ge4+ cations are incorporated in the studied GeO2-PbO glass system as GeO4 and GeO6 units. In this structure, PbO may also participate in the glass network with PbO4 structural units when the lead ion is linked to four oxygen atoms in a covalence bond configuration [18].

3- By addition of the lead oxide to glass composition up to 25 mole %, the intensity of absorption bands around 580 and 875 cm^{-1}, which are related to symmetric and anti-symmetric stretching vibration of the Ge-O-Ge of GeO4 tetrahedral units, decreases. In this condition, the intensity of the absorption band around 715 cm^{-1} which is related to the stretching vibration mode of the Ge-O-Ge bond in GeO6 octahedral units remains unchanged. On this basis, the conversion of GeO4 tetrahedra to GeO6 octahedra as well as increasing in the number of bridging oxygens upon increasing PbO occurs in the glassy network. On the other hand, by addition of PbO to GeO2 network up to 25 mole %, the density of non-bridging oxygens (NBO) will decrease and the glass network becomes more robust. Strengthening of the glassy network is the main reason of decreasing the λ0 toward shorter wavelengths as the PbO mole% content reaches to about 25 mole %.

4- By increasing the percentage of PbO beyond 25 mole %, the intensity of all absorption bands (around 500-700 and 700-1100 cm^{-1}) increases as a result of weakening the glass network (Fig. 5). This is the main reason for increasing the cut off wavelength toward longer wavelengths as the PbO content increases beyond 25 mole %.

The values of optical band gap energy (Eopt.) were determined for all prepared glasses using equation 1 [19, 20] and by extrapolation of the linear part of each curve it represents the variation of $(\alpha h\omega)^{1/2}$ with $h\omega$ to $(\alpha h\omega)^{1/2}=0$, as shown in Fig. 6.

$$\alpha h\omega = B(h\omega - E_{opt.})^n \qquad (1)$$

where α is the absorption coefficient, B is a constant, Eopt. is the optical band gap energy and n is an index which can have values of 1/2 and 2, depending on the nature of the inter-band electronic transitions for the absorption [21]. For n = 1/2 is associated with the allowed direct transitions and 2 is for the allowed indirect transitions.

Table 2. The optical absorption edge, λ0, optical energy gap (Eopt.) and optical band tail (ΔE) of GeO2-PbO glasses

S.N.	PbO mole %	λ0 (nm)	Eopt. (eV)		ΔE (eV)
			Direct	In-Direct	
	15	362±2	3.40±0.1	3.59±0.1	0.14±0.1
2	20	357±1	3.42±0.1	3.66±0.1	0.12±0.1
3	25	348±4	3.57±0.1	3.73±0.1	0.11±0.1
4	30	359±2	3.52±0.1	3.70±0.1	0.12±0.1
5	35	388±3	3.18±0.1	3.42±0.1	0.22±0.1
6	45	394±5	3.01±0.1	3.40±0.1	0.27±0.1
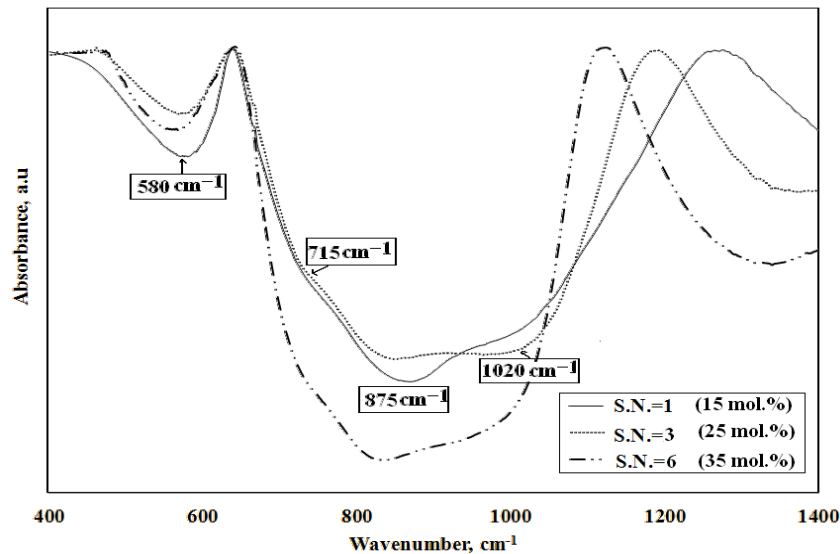
Fig. 5. The FTIR spectra of GeO2-PbO glasses with different percentages of PbO

Moreover, the values of Urbach energy (the width of band tails), ΔE, were estimated as the inverse slopes of the straight line of the curves, which represented the variation of $\ln\alpha$ versus $h\omega$ according to the following equation [22, 23]:

$$\alpha(\omega)=\alpha'(\omega)e(h\omega/\Delta E) \qquad (2)$$

where $\alpha'(\omega)$ is constant and ΔE is the width of the band tails energy. In fact, the width of the band tails is associated with valence and conduction bands were believed to be originated from electron transition between localized states. The width of these tails can be used to characterize the degree of disorder (defects concentration) in amorphous and crystalline solids. On the other hand, materials with larger value of ΔE would have a great tendency to convert weak bonds into defects.

In this regard, the obtained values of ΔE and Eopt. for all glassy specimens are presented in Table 2. According to this table, several points can be concluded:

1- The direct value of Eopt., for all prepared GeO2-PbO glasses, is lower than the indirect one. This indicates that optical absorption in GeO2-PbO system is associated with direct allowed transition.

2- By gradual increasing of the PbO content up to 25 mole %, the value of Eopt. increases from 3.40 to 3.57 eV. This result can be related to the enhancement in the number of bridging oxygens as well as glass network connectivity. However, the decrease in the Eopt. value beyond 25 mole % PbO can be related to the decrease in network connectivity and cross link density as maintained above.

3- The ΔE value (concentration of defects) of prepared GeO2-PbO glasses has minima at 25 mole % of PbO. This is in agreement with other achieved results and can be related to the minimum number of non-bridging oxygens in this composition.
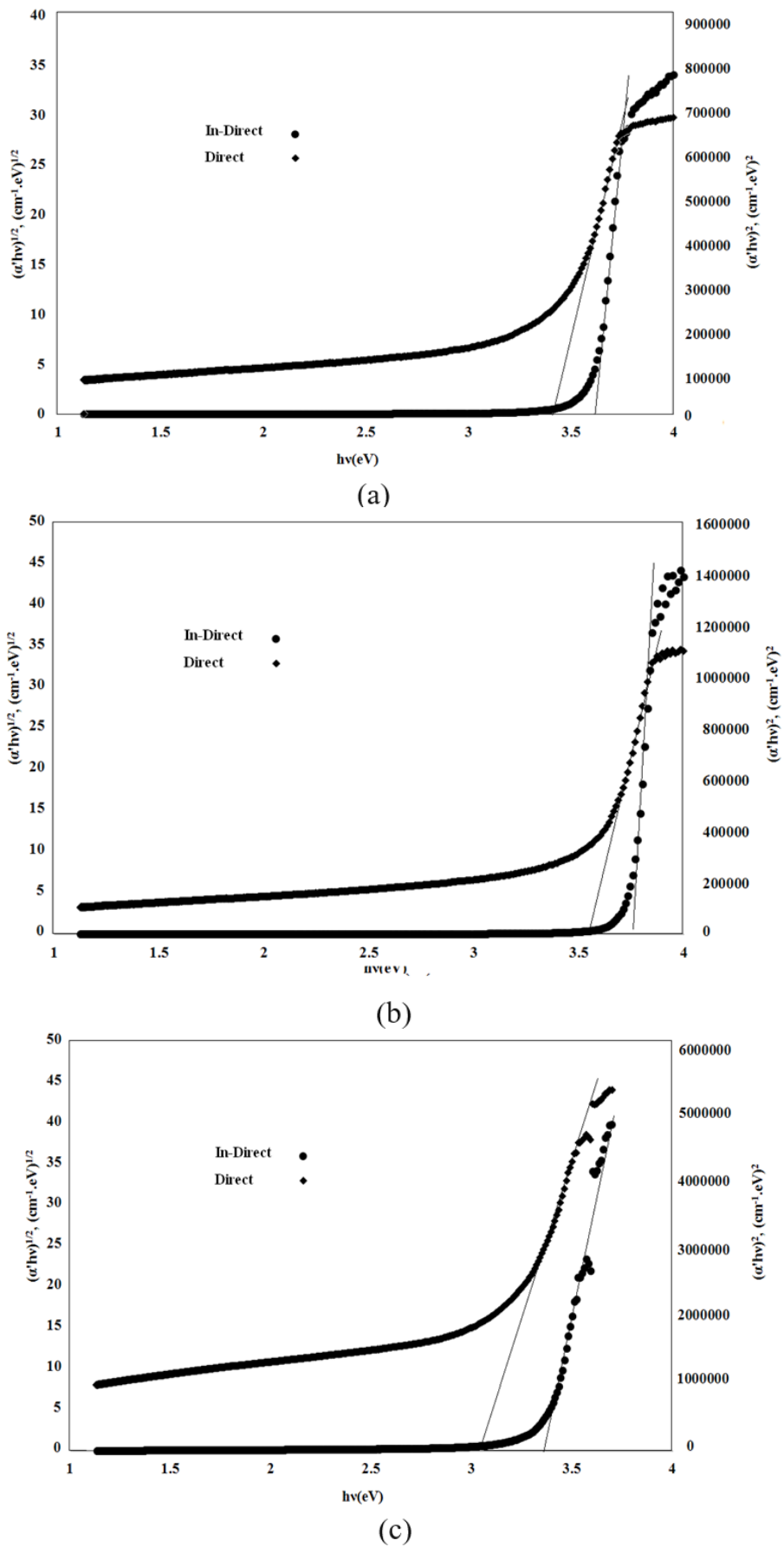
Fig. 6. Variation of (αhω)1/2 (direct) and (αhω)2 (indirect) against hω for GeO2-PbO glasses with a) S.N.=1, b) S.N.=3, c) S.N.=6

4- Conclusion

In this study, structural and optical characterization of bulk GeO2-PbO glasses was carried out. Based on the obtained results, fully amorphous phase can easily form in the GeO2-PbO system up to 45 mole % of PbO. Optical characteristization of GeO2-PbO glasses showed an anomalous behavior at 25 mole % of PbO for transmittance, absorption edge, optical energy gap and Urbach energy. This behavior is related to the conversion of GeO4-tetrahedra to GeO6-octahedra and the increase in the number of non-bridging oxygens upon increasing the PbO content up to 25 mole %.

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