



Thermal and optical properties of TeO₂–ZnO–BaO glasses

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ABSTRACT

We report the results of a systematic study of the thermal and optical properties of a new family of tellurite glasses, TeO₂–ZnO–BaO (TZBa), as a function of the barium oxide mole fraction and compare them with those of TeO₂–ZnO–Na₂O (TZN). The characteristic temperatures of this new glass family (glass transition, T_g , crystallization, T_x , and melting, T_m) increase significantly with BaO content and the glasses are more thermally stable (greater $\Delta T = T_x - T_g$) than TZN glasses. Relative to these, Raman gain coefficient of the TZBa glasses also increases by approximately 40% as well as the Raman shift from $\sim 680 \text{ cm}^{-1}$ to $\sim 770 \text{ cm}^{-1}$. The latter shift is due to the modification of the glass with the creation of non-bridging oxygen ions in the glass network. Raman spectroscopy allows us to monitor the changes in the glass network resulting from the introduction of BaO.

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1. Introduction

Among soft glasses, tellurites are attracting renewed interest for photonics applications. Most importantly, they transmit over a wide range of wavelengths, from 0.5 μm to 6 μm , are not photosensitive and offer the thermal and mechanical stability of oxide glasses [1–4]. In addition, they possess high linear and nonlinear refractive indices, low cut-off phonon energies around 750 cm^{-1} , high rare-earth solubility and a high Raman gain coefficient [5,6], all of which are important for applications, and in particular for the development of mid-IR fiber laser sources. Moreover, because of their wide glass-forming range, their composition can be adjusted to further optimize these optical properties. [7–9].

Pure TeO₂ cannot form a glass except under particular extreme conditions [10]. The addition of various modifiers increases the glass-forming range of tellurites. Binary tellurite glasses with alkali and alkaline earth additives have been studied extensively [11,12]. The addition of both ZnO and Na₂O to form the ternary TZN system increases the thermal stability of the tellurite glass and its resistance to devitrification. The most exhaustively studied composition in the TZN family is 75TeO₂–20ZnO–5Na₂O. It is found to possess good thermal stability ($\Delta T = 105^\circ\text{C}$) and a high refractive index ($n_0 \approx 2.0$). We have shown that an increase of the Na₂O content up to 10% (75TeO₂–15ZnO–10Na₂O) increases the stability of the glass and reduces the risk of crystallization during fiber drawing [13–15]. However, further addition of Na₂O beyond 10% reduces the glass transition temperature, leading to poor chemical durability and hindering practical usage for fiber lasers and amplifiers [16–18].

By contrast, addition of alkaline earth oxides like barium oxide has been shown to increase the transition temperatures and improve the thermal stability of tellurite glasses and, consequently the working range. Increasing the BaO content shifts the working transition temperatures towards higher values [9,19]. It also leads to an increase in the Raman gain coefficient and a larger spectral bandwidth compared to that of silica [20]. Previous studies have only reported results for single concentrations of BaO in tellurite glasses. In the present paper, we report the results of a more comprehensive study of the evolution of the physical and optical properties of TZBa glasses as a function of the BaO content.

2. Experimental details

All the glasses studied, (80– x)TeO₂–20ZnO– x BaO ($x = 5, 10, 15, 20 \text{ mol}\%$), were prepared by the standard melt-quenching method. High purity raw materials TeO₂(5 N), ZnO(5 N) and BaO(4 N) were weighed, mixed thoroughly, vacuum-dried and melted in gold crucibles at 850°C for 2 hrs in a flowing oxygen atmosphere. The melt was then poured onto preheated metal plates (230°C) and annealed below its glass transition temperature for 5 hrs in order to release thermal stresses. Annealed samples were then cut to the desired thickness and polished for optical measurements.

Thermal analysis was carried out on a Differential Scanning Calorimeter (TA instrument). The powder samples, approximately 20 mg in weight, were heated from 40°C to 600°C in a hermetically sealed aluminum pan under N₂ atmosphere. The glass transition temperature (T_g) was obtained by drawing tangents to the exothermic peak and the onset of crystallization (T_x) was taken as the temperature at which the heat flow starts to increase positively from its constant value.

Optical transmission was measured with a Perkin Elmer FTIR spectrometer in the range 1.8–25 μm using samples of approximately

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1 mm thickness. Refractive index measurements were done using a J.A. Woollam Variable Angle Spectroscopic Ellipsometer (VASE) in the wavelength range 290–1700 nm. At least three measurements were done on these samples and the average value was computed as a final result. Error bars indicate the scatter in the data. The Raman spectra were measured using a Horiba Jobin Yvon double monochromator Raman spectrometer at room temperature using an Ar-ion laser line at 488 nm.

3. Results

Fig. 1 shows the DSC trace of several TZBa glasses. T_g and T_x were found to increase with increase in BaO concentration. Table 1 quantifies the thermal properties of TZBa glasses.

FTIR measurements shown in Fig. 2 indicate that all our glasses have good transmission up to 5.5 microns.

Fig. 3a presents the refractive index dispersion measured with an ellipsometer and fitted with a Cauchy model. The variation in refractive index with increasing BaO concentration at $\lambda = 1550$ nm is shown in Fig. 3b. Table 2 quantifies the refractive index values at certain specific wavelengths.

Fig. 4 shows the deconvoluted Raman spectra measured in these glasses.

4. Discussion

4.1. (i) Thermal properties

One of the important parameters for the characterization of glassy materials is their T_g . With increasing BaO content from 5% to 20%, T_g and T_x were found to increase from 327 °C to 355 °C and 425 °C to 491 °C respectively. Also, the strength of the crystallization peak decreases with increasing BaO content and is almost absent for 20% BaO. These observations can be contrasted with the evolution of TZN glasses in which an increase in Na₂O content also results in the decreasing strength of the crystallization peak but a decrease of T_g and T_x rather than an increase. TZN glasses can be said to become more “fragile” [21] with increasing Na₂O while TZBa glasses become stronger with increasing BaO, though both increases have a tendency to prevent crystallization. Given the ionic radii of Na and Ba, 1 Å and 1.35 Å respectively, these results suggest that the opposite trend of T_g and T_x in both family of glasses is due to a difference in the free volume of the modified glass. In TZN, Na⁺ breaks Te—O bonds and opens the network while, in TZBa, Ba⁺⁺ also breaks Te—O bonds but forms tighter bonds with oxygen than Na⁺ and fills open spaces more completely in the network [22,23]. The suppression of crystallization

Table 1

Transition temperatures of TeO₂–ZnO–BaO glasses.

BaO concentration (mol. %)	T_g (± 2 °C)	T_x (± 2 °C)	$\Delta T = T_x - T_g$ (°C)
05	327	423	96
10	335	449	114
15	345	459	114
20	355	491	136

in both cases has therefore two different origins. In TZN, crystallization is suppressed because of bond breaking and an increase in free volume in a more open glass network while, in TZBa, it is suppressed because of a decrease in free volume and a more compact/dense glass (increased rigidity), making atomic and molecular rearrangements more difficult. In the glass transition range, the network normally acquires a higher degree of mobility that allows bond rearrangements or the transfer of covalent bonds between constituent atoms. The number of network bonds that must be rearranged or broken depends on the cross linking density of the network and the bond energy between constituent atoms. In TZBa, the glass transition temperature increases due to increased cross-linking density and bond strength between the atoms involved [24]. The relatively larger mass of barium atoms also reduces the free volume and favors cross-linking thus requiring more external energy for structural modifications. This in turn leads to an increase in T_g with increasing BaO concentration [16,23,25].

Thermal stability is an important issue in glass science for both fundamental and technological reasons. Thermal stability (ΔT) refers to the temperature range within which the glass does not tend towards devitrification ($T_x - T_g$): the higher the thermal stability, the better the glass quality. Drawing these glasses into optical fibers requires that they undergo repeated and prolonged heating cycles above T_g . If ΔT is low, thermal cycling leads to the formation of micro-crystals during fiber drawing, which acts as scattering centers and result in considerable attenuation of light. In general, ΔT should be ≥ 100 °C to avoid microcrystal formation. In Fig. 1, the addition of BaO is seen to result in shifting both T_g and T_x towards higher temperatures, with T_x shifting more than T_g , or equivalently ΔT increasing from 96 °C for 5% BaO to 136 °C for 20% BaO (Table 1). TZBa is therefore thermally more stable than TZN during processing of the glass, i.e. comparatively less prone to crystallization.

4.2. (ii) Optical properties

4.2.1. (a) FTIR spectroscopy

The FTIR spectra show a dip at around 3.3 microns which is due to the stretching vibrations of free OH groups [26]. These OH bands are a

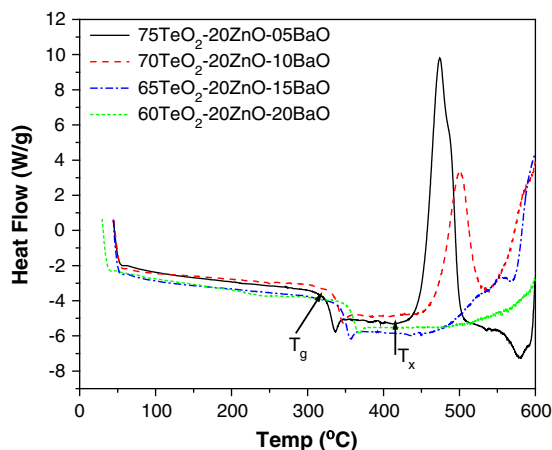


Fig. 1. DSC trace of TeO₂–ZnO–BaO glasses.

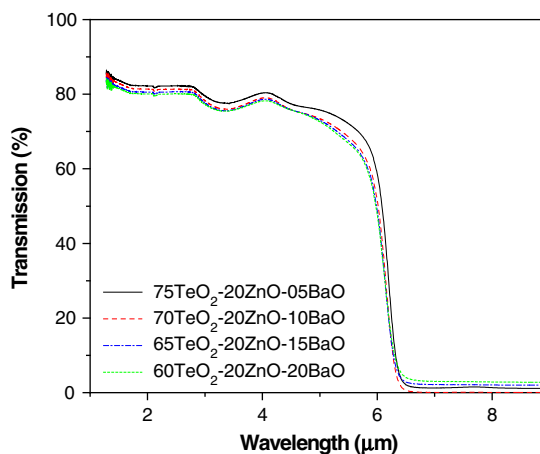


Fig. 2. FTIR spectra of TeO₂–ZnO–BaO glasses.

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