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Crystallization behaviour of $(1-x)TeO_2$–$xBaO$ ($x = 0.10$, 0.15 and 0.25 in molar ratio) glasses

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Abstract

The effect of BaO content on the crystallization of binary $(1-x)TeO_2$–$xBaO$ glasses (where $x = 0.10$, 0.15, 0.25 in molar ratio) was studied. Compositional dependence of the glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures were determined by DTA investigations in the temperature range between 25 and 900 °C with the heating rate of 10 °C/min. T_g temperatures shift to higher values with increasing BaO content. Crystallizing phases for each composition were characterized by XRD and SEM and their activation energies were determined by using the Ozawa and Kissinger methods.

Keyword: TeO_2-BaO glasses; Optical fiber amplifiers; Photonics materials

1. Introduction

In response of the huge amount of data transmission taking place worldwide, a substantial number of research investigations have been focused in improving the light transmission properties of optical fibers, optical properties of waveguide devices and quality of optical fiber amplifiers.[1–3] Thus, research efforts have been devoted to adjust and improve the gain spectra of Er-doped fiber amplifiers (EDFA).[1–3] Silica based fibers have the disadvantage of having high energy phonons, which limits the rare earth ions that could be used to optical amplification. In order to broaden the amplification bandwidth of rare earth-doped fibers, fluoride and some heavy metal oxides have been studied, which are known to have low energy phonons. Tellurite glasses are considered as good candidates for future photonics because they have a wide transmission window, good durability, high refractive index and comparatively low phonon energy. EDFA's with broader bandwidth have been manufactured using tellurite based fibers as erbium hosts.[4,5] Thus, more stable and efficient tellurite glass systems have been a very popular research topic lately.[6]

2. Experimental

2.1. Glass preparation

Transparent glasses were prepared with the compositions of $(1-x)TeO_2$–$(x)BaO$ where $x = 0.10$, 0.15 and 0.25 in molar ratio. All chemicals used were reagent grade of TeO_2 (99.999% purity, Aldrich Chemical Company) and $BaCO_3$ (98.5% purity, Lach-Ner, s.r.o.). The stoichiometric compositions of the batch materials (7 g) were well mixed thoroughly and the mixed raw materials were then heated in a platinum crucible up to 900–950 °C with a heating rate of 10 °C/min, to drive off CO_2. The resultant mixture was melted for about 1 h at the maximum temperature. The glasses were obtained by quenching the resulting melt by dipping the crucible into water.

2.2. Thermal analysis

The thermal behaviour of the glass samples was studied by differential thermal analysis (DTA) (Rigaku Thermal Analyzer). About 50 mg of the composition with $x = 10$ mol% and 120 mg of the other compositions were heated in a platinum crucible at heating rates of 5, 10, 15 and 20 °C/min in the 25–900 °C temperature range. Totally, there were 16 analyses for all compositions. The glass transition temperatures (T_g) and the crystallization temperatures (T_c) were determined from the tangent intersec-

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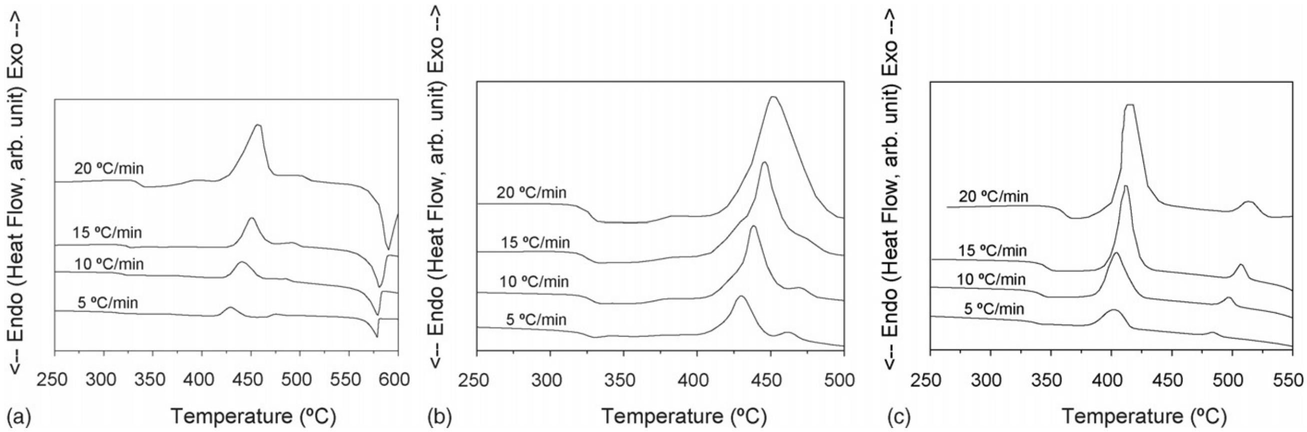


Fig. 1. (a) DTA curves of $0.90TeO_2$–$0.10BaO$ with different heating rates; (b) DTA curves of $0.85TeO_2$–$0.15BaO$ with different heating rates; (c) DTA curves of $0.75TeO_2$–$0.25BaO$ with different heating rates.

tions of the DTA curves. The melting temperatures (T_m) were obtained from the peak temperature of the endothermic peak.

2.3. Crystallization investigations

Crystallized samples were prepared for all crystal structures by heating up the glass samples up to 15–20 °C above the crystallization temperatures and holding them there for about 20 min. The pulverized samples of those crystallized structures were then investigated by X-ray diffraction (XRD) (Philips^{TM} Model PW3710) using Cu Kα radiation at 40 kV and 40 mA. Both surface and cross-section images were taken by Optical Microscope. Cross-sectional sides of the samples were prepared by cutting and polishing the rough surfaces, whereas the surfaces were investigated without any treatment. SEM investigations were conducted in a JROL^{TM} Model JSM-T330 operated at 25 kV and linked with a Zmax 30 Boron-up light element energy dispersive spectrometer (EDS) detector.

3. Results and discussions

3.1. DTA and thermal stability

The DTA curves given in Fig. 1 reflect the typical nature of a normal glass with a small broad endothermic peak, representing the glass transition temperature (T_g), crystallization peaks and eventually the endothermic melting peak, respectively. All of the three compositions ($x = 10$, 15 and 25 mol%) showed two crystallization peaks. As Table 1 reveals, first crystallization temperature for different compositions was found in the range of 392–446 °C, whereas the second ones vary from 461 to 487 °C. The parameter $\Delta T(T_c - T_g)$ is normally used to evaluate the glass stability against crystallization.[7] As can be seen in Fig. 1, the ΔT value decreases with increasing BaO content for a constant heating rate. The most stable glass in this system is the $0.90TeO_2$–$0.10BaO$ and has a ΔT value of 123 °C.

The glass stability can also be evaluated using the Hruby parameter, K_{gl},[8] given by

$$K_{gl} = \frac{T_x - T_g}{T_m - T_x} \quad (1)$$

In the present investigations the calculations were made according to the values obtained by the heating rate of 10 °C/min. It was proved that for thermally stable glass forming systems the value of K_{gl} is more than 0.1[9] and hence thermally stable glass forming systems are characterized by high values of K_{gl} and vice versa. The system showed a decrease in the value of K_{gl} with the increase of the BaO content. Using the Hruby parameter, the $0.90TeO_2$–$0.10BaO$ glass can be found as the most stable glass in this system and has a K_{gl} value of 0.91.

3.2. Crystallization investigations

Fig. 2(a–c) shows the respective XRD patterns of the $0.90TeO_2$–$0.10BaO$, $0.85TeO_2$–$0.15BaO$ and $0.75TeO_2$–$0.25BaO$ glasses heat treated at two different temperatures above the peak crystallization temperatures given in Fig. 1 for a heating rate of 10 °C/min. Fig. 2(a) reveals the patterns of the $0.90TeO_2$–$0.10BaO$ sample which are almost identical whereas there are differences of intensities between the dom-

Table 1
Glass transition (T_g) and crystallization temperatures (T_{c1} and T_{c2}) of the $0.90TeO_2$–$0.10BaO$, $0.85TeO_2$–$0.15BaO$ and $0.75TeO_2$–$0.25BaO$ glasses scanned at the heating rates of 5, 10, 15 and 20 °C

BaO (mol%)	5 °C/min			10 °C/min			15 °C/min			20 °C/min		
	T_g	T_{c1}	T_{c2}	T_g	T_{c1}	T_{c2}	T_g	T_{c1}	T_{c2}	T_g	T_{c1}	T_{c2}
10	314	431	485	323	446	482	329	458	495	323	429	482
15	316.5	410	449	322	412	461	324	417		319	424	
25	329	382	475	332.5	389	487	333	395	500	338	394	516

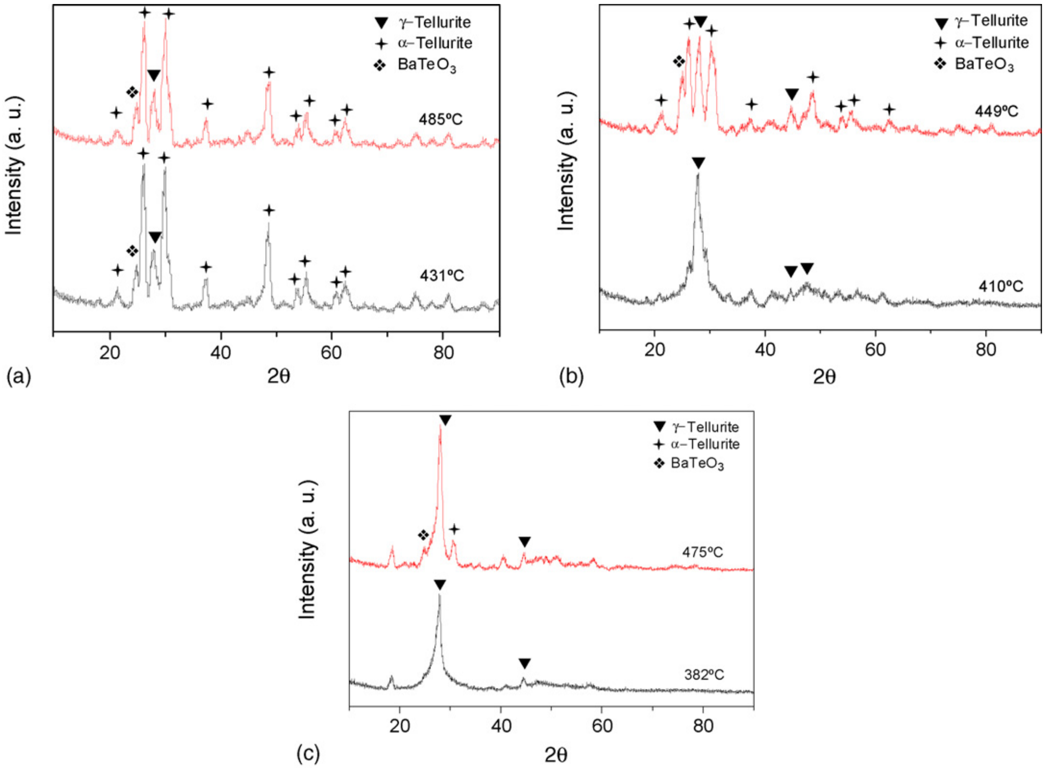


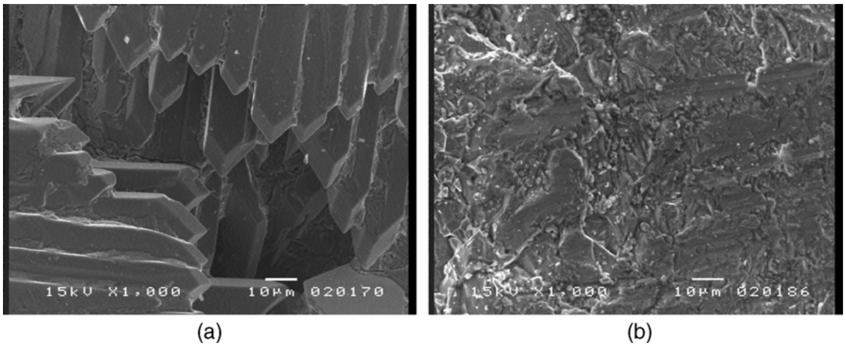
Fig. 2. (a) XRD patterns of crystallized $0.90TeO_2$–$0.10BaO$ glass sample; (b) XRD patterns of crystallized $0.85TeO_2$–$0.15BaO$ glass sample; (c) XRD patterns of crystallized $0.75TeO_2$–$0.25BaO$ glass sample.

inant peaks of each one. The peaks of α-tellurite (tetragonal structure with lattice parameters $a = 4.81$ Å, $c = 7.61$ Å[10]) are visible at 26°, 30° and 48° which are characteristic are for this structure. However, there is a completely different behaviour by the $0.85TeO_2$–$0.15BaO$ sample. It is obvious in Fig. 2(b) that there is a significant structural change between the patterns. At 449 °C, the characteristic angles 26°, 30° and 48° become visible. The dominant γ-tellurite (orthorhombic structure with lattice parameters $a = 5.607$ Å, $b = 12.034$ Å and $c = 5.463$ Å[11]) peak by 28 °C which is visible at the lower temperature did not disappear but it lost some intensity by the second crystallization.

However, the system shows almost no structural change between the two patterns of $0.75TeO_2$–$0.25BaO$ sample taken at different temperatures. In Fig. 2(c) the pattern at the lower temperature reveals one dominant peak which is the characteristic peak of the polymorph, γ-tellurite phase. At the higher temperature, almost the same picture is observed whereas there is a slight change between the two patterns.

3.3. SEM/EDS investigations

Fig. 3(a) shows the SEM micrograph taken from the surface of the sample with 10 mol% BaO content. In this micrographs, the dendrites are clearly visible and show that the crystallization propagates in one direction. EDS studies of the SEM micrographs seen in Fig. 3(a) revealed that there is almost no Ba content on those dendritic structures which means that there is an almost complete TeO_2 crystallization on these surfaces.



(a) (b)

Fig. 3. (a) SEM micrographs taken from the surface crystalline region with 1000 magnification of the $0.90TeO_2$–$0.10BaO$ sample heated to 485 °C followed by quenching in air; (b) SEM micrographs taken from the cross-section crystalline region of the $0.90TeO_2$–$0.10BaO$ sample heated to 485 °C followed by quenching in air.

This is not the case for the cross-section crystalline region of the sample seen in Fig. 3(b). There are no dendritic structures on the cross-section. EDS studies showed that there is about 11 wt.% Ba on the cross-section. A similar behaviour was observed in the samples containing other BaO contents.

3.4. Crystallization kinetics

The Avrami constants n were found as 1.55, 1.66, and 2.08 for the $0.90TeO_2$–0.10BaO, $0.85TeO_2$–0.15BaO, and $0.75TeO_2$–0.25BaO samples, respectively. These values should be rounded up to 2, meaning that there is two-dimensional surface crystallization. The related activation energies (Q) were calculated as 311, 465.8 and 493.6 kJ/mol for the first crystallizations of $0.90TeO_2$–0.10BaO, $0.85TeO_2$–0.15BaO and $0.75TeO_2$–0.25BaO samples, respectively.

4. Conclusions

(a) The most stable glass in this system has a ΔT value of 123 °C and a K_{gl} value of 0.91. The system showed a decrease in the value of both ΔT and K_{gl} with the increase of BaO content.

(b) XRD patterns of the $0.90TeO_2$–0.10BaO sample showed α-tellurite as the dominant phase. A completely different behaviour was seen $0.85TeO_2$–0.15BaO sample which shows γ-tellurite as a dominant structure. By the second crystallization, the system converts partially to α-tellurite. The last composition which has 25 mol% BaO shows only the characteristic peak of the polymorph γ-tellurite by both crystallization patterns.

(c) SEM investigations revealed the dendritic crystallizations on the sample surfaces. With the help of energy dispersive spectrometry (EDS), the crystallization of TeO_2 was found to be dominantly on surfaces.

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References

1. Sandoe, J. N., Sarkies, P. H. and Parke, S., *J. Phys. D*, 1972, **5**, 1788.
2. Miniscalco, W. J., *IEEE J. Lightwave Technol.*, 1991, **LT-9**, 234.
3. Semenkoff, M., Guibert, M., Ronarch, D., Sorel, Y. and Kerdiles, J. F., *J. Non-Cryst. Solids*, 1995, **184**, 240.
4. Ohishi, Y., Mori, A., Yamada, M., Ono, H., Nishida, Y. and Oikawa, K., *Opt. Lett.*, 1998, **23**, 274.
5. Mori, A., Sakamoto, T., Kobayashi, K., Shikano, K., Oikawa, K., Oshino, K. *et al.*, *IEEE J. Lightwave Technol.*, 2002, **LT-20**, 822.
6. Wang, J. S., Vogel, E. M. and Snitzer, E., *Opt. Mater.*, 1994, **3**, 187.
7. Murugan, G. S. and Ohishi, Y., TeO_2–BaO–SrO–Nb_2O_5 glasses: a new glass system for waveguide devices applications. *J. Non-Cryst. Solids*, 2004, **341**, 86–92.
8. Hruby, A., *Czech. J. Phys. B*, 1972, **32**, 1187.
9. Thornburg, D. D., *Mater. Res. Bull.*, 1974, **9**, 1481.
10. JCPDS-ICDD 42-1365.
11. JCPDS-ICDD 9-433.