Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 1801–1804
www.elsevier.com/locate/jeurceramsoc

Microstructural characterization of $(1-x)TeO_2$–$xPbF_2$ ($x = 0.10$, and 0.25 mol) glasses

M.L. Öveçoğlu [a], İ. Kabalcı [b,*], G. Özen [b], B. Öz [a]

[a] *Department of Metallurgical & Materials Engineering, Faculty of Chemical & Metallurgical Engineering, Istanbul Technical University, Maslak 34469, İstanbul, Turkey*
[b] *Department of Physics, Istanbul Technical University, Maslak 34469, İstanbul, Turkey*

Available online 12 June 2006

Abstract

Thermal and microstructural characteristics of $(1-x)TeO_2$–$xPbF_2$ ($x = 0.1$, and 0.25) optical glasses were investigated. A differential thermal analysis technique was used to determine the glass transitions, crystallization and melting temperatures of each composition. Each sample shows only one crystallization peak at 355 and 322 °C for 0.1 and 0.25 mol PbF_2 content, respectively. Microstructural analysis of the samples was carried out after the samples annealed above their crystallization temperatures. The X-ray diffraction pattern of the sample containing 0.1 mol PbF_2 content predicts that the $PbTe_3O_7$, and γ-TeO_2 crystalline phases are present. The micrographs of the samples, and the elemental analysis of the crystalline phases observed were recorded using an optical microscope (OM). These results verify the existence of the crystalline phases determined from the X-ray diffraction patterns.

Keyword: Optical properties

1. Introduction

The synthesis of the glasses with high refractive index values is of great importance in the glass science; hence tellurium dioxide (TeO_2) based glasses are of scientific and technical interest on account of their various unique properties.[1] They have been considered as promising materials for fiber-optic amplifiers and fiber lasers. In comparison with silicate and borate glasses that are in use commercially, tellurite glasses have also more advantages as frequency up conversion laser hosts due to their physical properties such as low melting temperature, high dielectric constant, high refractive index, large third-order nonlinear susceptibility, better infrared transmissivity, low phonon energies, and therefore, glass have small multi-phonon decay rates for the excited states when they are doped with the rare earth ions.[2–4] In addition, tellurite glasses are resistant to atmospheric moisture and capable of incorporating large concentrations of rare earth ions such as Tm^{3+} into the matrix. The refractive index, n, and density, ρ, for many oxide glasses can be varied by changing the glass composition, sample temperature, pressure, and transformation range history such as reannealing.[4,5]

Microstructure of the materials used as amplifiers in infrared region is a very important parameter since it directly affects the luminescence quantum efficiency as reported in the study of the optical properties of Er^{3+}-doped TeO_2–PbF_2 glasses.[4] The present study is part of an ongoing investigation on the $(1-x)TeO_2$–$xPbF_2$ glasses doped[5] with 1.0 mol% Tm_2O_3. After a series of preliminary DTA and X-ray diffractometry tests, two compositions, with 0.1, and 0.25 mol PbF_2 component were chosen to investigate the effect of the PbF_2 content on the microstructure of this glass matrix.

2. Experimental

2.1. Glass synthesis

Two tellurite samples were prepared to with the compositions of 90 mol% TeO_2–10 mol% PbF_2, and 75 mol% TeO_2–25 mol% PbF_2 (now hereafter referred to as the $0.9TeO_2$–$0.1PbF_2$, and $0.75TeO_2$–$0.25PbF_2$). All chemicals used in this investigation were reagent grade of TeO_2 (99.999% purity, Aldrich Chemical Company), and PbF_2 (99% purity, Aldrich Chemical Company). Batches of 7 g in size were thoroughly mixed and melted in

* Corresponding author at: Department of Physics, Harran University, 63100 Şanlıurfa, Turkey. Tel.: +90 212 285 3206; fax: +90 212 285 6386.
E-mail address: kabalci@itu.edu.tr (İ. Kabalcı).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.04.161

a platinum crucible with a closed lid in an electrically heated furnace at 800 °C for 1 h. The melts then were removed from the furnace and quenched in air by casting and pressing between two rectangular graphite slabs at room temperature.

2.2. Thermal behavior and microstructural characterization

Differential thermal analysis (DTA) scans of as-cast glass specimens were carried out in a Rigaku Thermoflex thermal analyzer equipped with a PTC-10A temperature control unit in order to determine the characteristic glass transition temperatures, T_g, crystallization onset, T_c, and the peak crystallization temperatures, T_p. The samples, about 20 mg, static non-isothermal DTA experiments were performed by heating at heating rate of 10 °C/min in a platinum crucible and using the same amount of Al_2O_3 as the reference material in the temperature range between 20 and 600 °C. The crucibles used were matched pairs made of platinum and the temperature precision was ±1 °C. The T_g temperature is selected as mid-point between the onset and the minimum temperature. The T_c temperature is measured at the onset crystallization, and the T_p temperature is measured at the peak of crystallization. The samples were annealed above their crystallization peak temperatures using a muffle furnace with heating rate 10 °C/min.

The microstructural characterization of the as-cast and annealed glass samples were carried out using X-ray diffraction (XRD) and optic microscopy (OM) techniques. The X-ray diffraction investigations were carried out in a Philips™ Model PW3710 using Cu Kα radiation at 40 kV and 40 mV settings in the 2θ range from 10° to 90°. The crystallized phases were identified by comparing the peak positions and intensities with those in the JCPDS (Joint Committee on Power Diffraction Standards) data files.[6,7] The Nikon Eclipse L150 Optical Microscope (OM) was used to obtain the optical micrographs of the samples surfaces.

3. Results and discussion

Fig. 1 gives the DTA curves of the glasses scanned at a rate of 10 °C/min between 250 and 600 °C. DTA scans exhibit a small endothermic peak called as the glass transition temperatures, T_g, at 302 and 275 °C for the glasses with the 0.1 and 0.25 mol PbF_2 component. The T_g values determined in this investigation are higher than those reported by Silva et al.[8,9] They characterized the thermal properties of the glasses with a differential scanning calorimeter (DSC) for the $(1-x)TeO_2$–$xPbF_2$ glass using the heating rate as 10 °C/min. As seen in Fig. 1(b), T_g shifts to lower values with the increasing PbF_2 content. This expected behavior is attributed to the fact that PbF_2 acts as a network modifier and breaks down the TeO_4 network structure.[12]

XRD technique is widely being used to identify the crystalline phases in glasses.[9] TeO_2 is known to crystallize in two stable phases known as α-TeO_2 and β-TeO_2. The α-TeO_2 phase was observed in TeO_2–PbF_2 binary glass system by Silva et al.[9] They were able to determine the α-TeO_2 and $PbTe_3O_7$ crystalline phases when they varied the PbF_2 content from 0.1 to 0.25 mol.

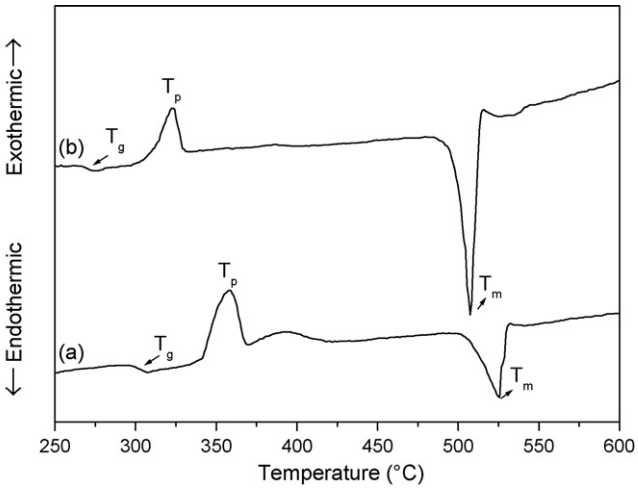

Fig. 1. DTA graph of: (a) $0.9TeO_2$–$0.1PbF_2$ glass and (b) $0.75TeO_2$–$0.25PbF_2$ glass recorded with a heating rate of 10 °C/min (T_g, T_p, and T_m are the glass transition, the crystallization and melting temperatures, respectively).

They also reported that $PbTe_3O_7$ crystalline phase decomposes into α-TeO_2 crystalline phase in which lead participates to the glassy network formation. Blanchandin et al. also studied TeO_2 based glass systems.[10–12] They observed the formation of the two unstable crystalline phases called γ-TeO_2 and δ-TeO_2 in addition to the stable α-TeO_2 crystalline phase.

Fig. 2 reports the XRD patterns of our samples together with the α-TeO_2 crystalline phase. Fig. 2(b) is the XRD pattern of the $0.9TeO_2$–$0.1PbF_2$ glass sample measured after the sample was annealed at 370 °C for 30 min. The XRD pattern of $0.75TeO_2$–$0.25PbF_2$ glass sample recorded after the sample was annealed at 340 °C for 30 min is given in Fig. 2(c). The 2θ and the I/I_{max} values were determined from the XRD measurements and listed in Table 1. The crystalline phases observed in our samples were identified by comparing the measured 2θ and the I/I_{max} values with the ones reported in the literature.[13]

As can be seen from Fig. 2, the X-ray pattern of the sample containing 0.1 mol PbF_2 predicts that the crystalline phase are

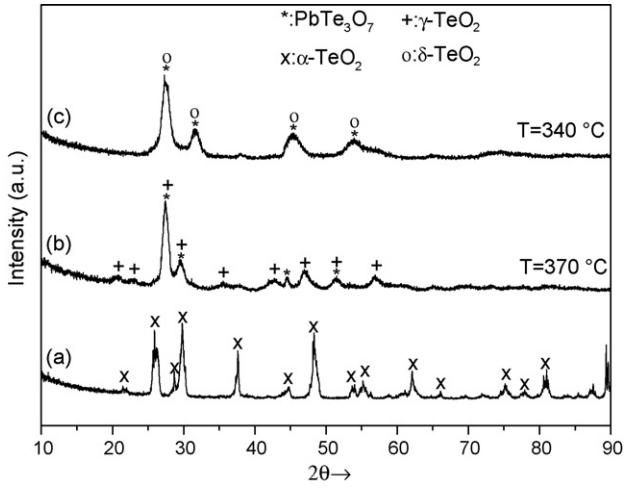

Fig. 2. XRD patterns of: (a) α-TeO_2 crystal, (b) $0.9TeO_2$–$0.1PbF_2$ glass annealed 370 °C for 30 min and (c) $0.75TeO_2$–$0.25PbF_2$ glass annealed at 340 °C for 30 min.

Table 1
The 2θ and the I/I_{max} values were determined from the XRD measurements for the $0.9TeO_2$–$0.1PbF_2$ (annealed at 370 °C for 30 min), and $0.75TeO_2$–$0.25PbF_2$ (annealed at 340 °C for 30 min) glasses

$0.9TeO_2$–$0.1PbF_2$ glass		$0.75TeO_2$–$0.25PbF_2$ glass	
2θ	Intensity (%)	2θ	Intensity (%)
21.266	18.48	27.48	100
23.4	17.21	31.82	41.98
27.42	100	38.16	11.57
29.68	36.25	45.6	35.37
31.48	11.85	54.36	28.09
35.54	14.1		
38.2	9.309		
43.04	15.94		
44.64	18.62		
47.04	25.25		
51.54	16.93		
56.9	20.31		

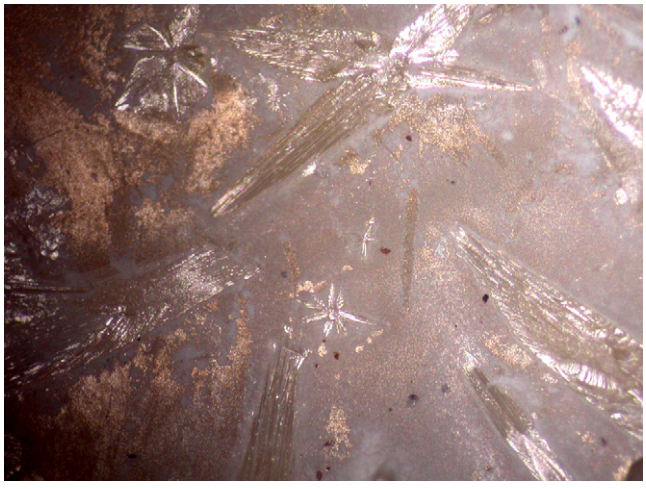

Fig. 3. A representative micrograph of the $0.9TeO_2$–$0.1PbF_2$ glass annealed at 370 °C for 30 min taken with an optical microscope.

Fig. 4. A representative micrograph of the $0.75TeO_2$–$0.25PbF_2$ glass sample annealed at 340 °C for 30 min taken with an optical microscope.

$PbTe_3O_7$ and δ-TeO_2. The pattern of the sample with 0.25 mol PbF_2 content shows the existence of the $PbTe_3O_7$ and δ-TeO_2 crystalline phases.

The micrograph of the sample with 0.1 mol PbF_2 content taken using the optical microscope is presented in Fig. 3. This picture shows the presence of the γ-TeO_2 phase in this composition. On the other hand as seen in Fig. 4 the sample with 0.25 mol PbF_2 content contains the δ-TeO_2 meta-stable crystalline phase.

4. Conclusion

On the basis of the results reported in the present investigation, the following conclusions can be drawn:

1. DTA results obtained with a heating rate of 10 °C/min show that the peak crystallization temperature decreases from 355 to 322 °C as the PbF_2 content increases from 0.1 to 0.25 mol.
2. The XRD pattern of the sample with the 0.1 mol PbF_2 content reveals that the exotherm above the glass transition temperature is associated with the crystallization of the $PbTe_3O_7$ and γ-TeO_2 phases. On the other hand, the XRD pattern of the sample with 0.25 mol PbF_2 content predicts the existence of the $PbTe_3O_7$ and δ-TeO_2 crystalline phases.
3. The micrographs recorded using an optical microscope give information about the size and the microstructure of the crystalline phases identified using the XRD records.

Acknowledgements

This research has been supported by the Institute of Science and Technology of İstanbul Technical University under the project number 30899 and Harran University under the project number 392.

References

1. Wang, J. S., Vogel, E. M. and Snitzer, E., Tellurite glasses: a new candidate for fiber devices. *Opt. Mater.*, 1994, **3**, 187–203.
2. Chowdari, B. V. R. and Kumari, P. P., Studies on $Ag_2O{\cdot}M_xO_y{\cdot}TeO_2$ ($M_xO_y = WO_3, MoO_3, P_2O_5$ and B_2O_3) ionic conducting glasses. *Solid State Ionics*, 1998, **113–115**, 665–675.
3. Stanworth, J. E., Tellurite glasses. *Nature*, 1952, **169**, 581–582.
4. Xu, S., Wang, G., Zhang, J., Dai, S., Hu, L. and Jiang, Z., Composition dependent upconversion of Er^{3+}-doped PbF_2–TeO_2 glasses. *J. Non-Cryst. Solids*, 2004, **336**, 230–233.
5. Sennaroglu, A., Kabalci, I., Kurt, A., Demirbas, U. and Özen, G., Spectroscopic properties of Tm^{3+}: TeO_2–PbF_2 glasses. *J. Lumin.*, 2005, **116**, 79–86.
6. Powder Diffraction File, Card no. 37-1392, 1992 Database Edition, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA.
7. Powder Diffraction File, Card no. 42-1365, 1992 Database Edition, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA.
8. Champarnaud-Mesjard, J. C., Blanchandin, S., Thomas, P., Mirgorodsky, A. P., Merle-Mejean, T. and Frit, B., Crystal structure, Raman spectrum and lattice dynamics of a new metastable from of tellurium dioxide: γ-TeO_2. *J. Phys. Chem. Solids*, 2000, **61**, 1499–1507.

9. Silva, M. A. P., Poulain, M., Messaddeq, Y. and Ribeiro, S. J. L., Lead–cadmium oxyfluoride glasses and glass-ceramics. *J. Optoelectron. Adv. Mater.*, 2002, **4**(3), 799–808.
10. Marjanavic, S., Toulouse, J., Jain, H., Sandmann, C., Dierolf, V., Kortan, A. R., Kopylov, N. and Ahrens, R. G., Characterization of new erbium-doped tellurite glasses and fibers. *J. Non-Cryst. Solids*, 2003, **322**, 311–318.
11. Blanchandin, S., Marchet, P., Thomas, P., Champarnaud-Mesjard, J. C. and Frit, B., New investigations within the TeO_2–WO_3 system: phase equilibrium diagram and glass crystallization. *J. Mater. Sci.*, 1999, **34**, 4285–4292.
12. Silva, M. A. P., Messaddeq, Y., Ribeiro, S. J. L., Poulain, M., Villain, F. and Briois, V., Structural studies on TeO_2–PbO glasses. *J. Phys. Chem. Solids*, 2001, **62**, 1055–1060.
13. Tromel, M., Burckhardt, H. G., Heydarian, H., Hutzler, F. W. and Munch, E., *Acta Crystallogr. A*, 1982, **40**, 216.