

The preparation and structural studies in the $(80 - x)\text{TeO}_2-20\text{ZnO}-(x)\text{Er}_2\text{O}_3$ glass system

M.R. Sahar *, K. Sulhadi, M.S. Rohani

Advanced Optical Material Research Group, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai, Johor DT, Malaysia

Available online 26 November 2007

Abstract

Er^{3+} -doped tellurite glasses of the $(80 - x)\text{TeO}_2-20\text{ZnO}-(x)\text{Er}_2\text{O}_3$ system ($0.5 \text{ mol}\% \leq x \leq 2.5 \text{ mol}\%$) have successfully been made by melt-quenching technique and their structure has been investigated by means of DTA and Raman spectroscopy. The DTA results show the thermal parameters; such as the glass transition temperature (T_g) and crystallization temperature (T_c) were determined. It is found that this system provides a stable and wide glass formation range in which the glass stability around 99–140 °C may be obtained. The Raman spectroscopy used the structural studies in the glass system. Two Raman shift peaks were observed around 640–670 cm^{-1} and 720–740 cm^{-1} , which correspond to the stretching vibration mode of TeO_4 tbp and TeO_3 tp, respectively. It is found that the spectral shift in Raman spectra is depending on the Er_2O_3 content. This evolution is an indication of the changes in the basic unit of the glass structure. © 2007 Elsevier B.V. All rights reserved.

Keywords: Raman spectroscopy; Oxide glasses; Tellurites; Rare-earths in glasses; Structure; Thermal properties

1. Introduction

The emission characteristics of laser glass are largely dominated by their structure and the site state of their doping ions. Presently, only rare earth ions are known to perform the lasing action in glassy hosts [1]. It has been described elsewhere that the TeO_2 – ZnO glass system exhibits a unique optoelectronic properties [2] and was used as laser light modulators [3]. It has also been reported that the glass is suitable as a host for optically active rare earth ions [4] and the emission from a fabricated double-clad Er^{3+} -doped tellurite single mode fibers, has a potential use for fiber lasers and optical amplifier [5]. Since then, the Er^{3+} -doped tellurite glasses have been a major attractive research subjects for the up-conversion emission due to their low phonon energy [6]. Meanwhile, the structural and the glass formation of tellurite glass has extensively been studied by Burger et al. [7] and the Raman spectral which is a linear evolution of the glass network with com-

position has been studied by Charton et al. [8]. However, not many researches on the characteristics of the glass doped with Er_2O_3 have been reported in the literature. It is therefore the aim of this paper to report the latest development on the structural properties of the glass. All the results will be discussed with respect to their composition.

2. Experimental

The Er^{3+} -doped tellurite glass of $(80 - x)\text{TeO}_2-20\text{ZnO}-(x)\text{Er}_2\text{O}_3$ system ($0.5 \text{ mol}\% \leq x \leq 2.5 \text{ mol}\%$) was prepared by melt quenching technique. Batches of 20 g were prepared from reagent grade powders of TeO_2 (purity 99%), ZnO (purity 99%) and Er_2O_3 (purity 99.9%). A well-mixed mixture was preheated at 400 °C before being melted in silica crucible at 900 °C for 1 h. After a required viscosity is achieved, the melts is quenched between two brass plates followed by annealing at 200 °C for 3 h before allowed to cool down to room temperature.

DTA (differential thermal analyser) Perkin Elmer 7 series was used to determine the thermal parameters, such as glass transition (T_g) and crystallization temperature (T_c) of the glass.

* Corresponding author. Tel.: +6075534184; fax: +6075566162.
E-mail address: m-rahim@dfiz2.fs.utm.my (M.R. Sahar).

A Perkin Elmer GX FT Raman spectroscopy has been used to get the Raman spectra. An analysis is done at 810 nm using a relatively fine glass powder with a targeted power laser of about 350 nW. Raman spectra were recorded in the range from 100 to 2000 cm^{-1} .

3. Results

Series of glasses have successfully been made and their composition, are listed in Table 1. From Table 1, it can be seen that a stable and wide glass formation range may

Table 1
A typical glass composition and their respective thermal parameter, with errors ± 0.01 °C

Composition (mol%)			Temperature (± 0.01 °C)		
TeO ₂	ZnO	Er ₂ O ₃	T _g	T _c	T _c -T _g
80.0	20.0	0.0	325.00	439.00	114.00
79.5	20.0	0.5	321.00	420.00	99.00
79.0	20.0	1.0	322.00	442.00	120.00
78.0	20.0	2.0	323.00	460.00	137.00
77.5	20.0	2.5	335.00	475.00	140.00

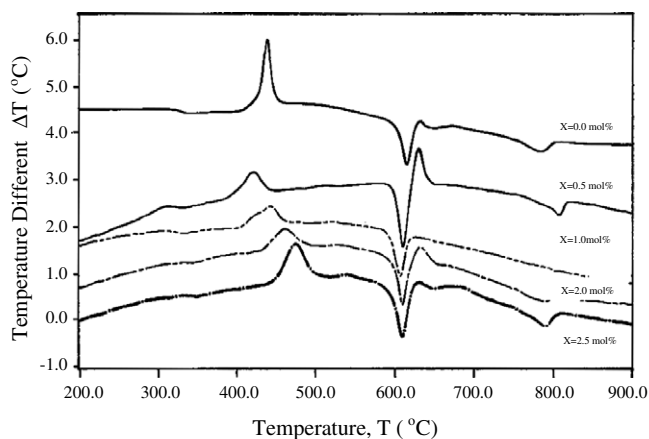


Fig. 1. DTA curve of $(80-x)\text{TeO}_2-20\text{ZnO}-(x)\text{Er}_2\text{O}_3$ glasses with various compositions.

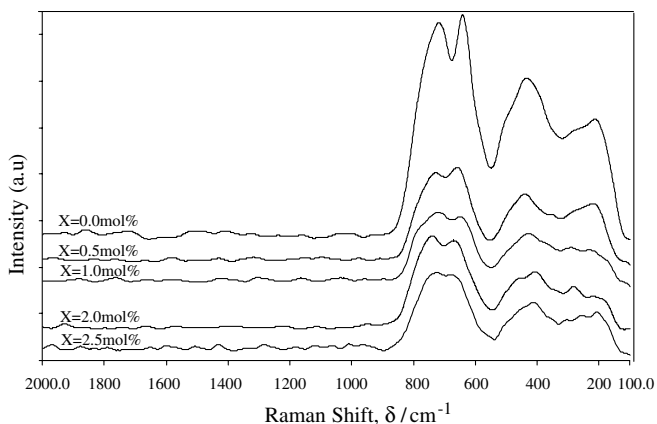


Fig. 2. The Raman spectra of $(80-x)\text{TeO}_2-20\text{ZnO}-(x)\text{Er}_2\text{O}_3$ glasses with various compositions.

Table 2

The Raman peaks positions of the tellurite glass system, with errors ± 1 cm^{-1}

Composition (mol%)			Raman shift
TeO ₂	ZnO	Er ₂ O ₃	$\delta \pm 1$ (cm^{-1})
80.0	20.0	0.0	433; 642; 720
79.5	20.0	0.5	433; 651; 725
79.0	20.0	1.0	293; 424; 651; 725
78.0	20.0	2.0	280; 412; 671; 733
77.5	20.0	2.5	260; 412; 671; 733

be obtained. Meanwhile, the DTA curves obtained from some samples are shown in Fig. 1. From Fig. 1, the peaks existence of T_g and T_c are well defined. Together with T_c-T_g, these peaks are inserted in Table 1.

The Raman spectra of all samples are shown in Fig. 2 and their peak shifts are summarized in Table 2. From Fig. 2, it can clearly be seen that the peaks around 410–440 cm^{-1} occur in all glasses. However, when the Er₂O₃ content is being increased more than 0.5 mol%, the Raman intensity around 640–670 cm^{-1} decreases while the intensity around 720–740 cm^{-1} increases.

4. Discussion

As can be seen from Table 1, an addition of small amount of Er₂O₃ (up to 0.5 mol%) would result in the decrease of glass stability (as indicated by T_c-T_g). The decrease in stability is presumably due to the decrease in the rigidity of glass network [9]. However, as the addition of Er₂O₃ is further increase, the rigidity of glass network increases, thus increasing the glass stability. This is presumably due to the participation of Er³⁺ in the glass network [10].

From Table 1, it can be observed that there is a linear relationship between T_c-T_g and T_c against the Er₂O₃ content. This indicates that the glass is easily fabricated [11]. The increase in glass stability is also reported to be due to the structural formation of ZnTeO₃ units [12].

The study on the structure of TeO₂-based glasses by Raman spectroscopy has been reported by many workers [8,10,13–17]. As shown in Fig. 2, there are two pronounce peaks occur around 640–670 cm^{-1} and 720–740 cm^{-1} . The peak intensity around 640–670 cm^{-1} , which is assigned to a stretching vibration of TeO₄ tbp (trigonal bipyramids) units was observed to decrease as the Er₂O₃ contents increases. The decrease in intensity would suggest the possibility of conversion from TeO₄ tbp units to the other basic structural unit [14]. The peak around 720–740 cm^{-1} were reported to be due to the perturbation of TeO₄ tbp units into TeO₃ tp (trigonal pyramids) units via the intermediate coordination of TeO₃₊₁ [8,10,14]. Both features would clearly indicate that the network of the TeO₃ tp structural unit increases with the increasing of Er₂O₃ contents.

Other peaks around 410–440 cm^{-1} , are observed to be less sensitive to the Er₂O₃ contents. A decrease in the peak intensity would suggest the occurrence of the destruction

of Te–O–Te (or O–Te–O) in the linkages [6], thus resulted in the decreasing of the Te–O–Te linkages in a continue network of TeO_n ($n = 4, 3 + 1$, and/or 3) entities, which is consistent with the observation reported elsewhere [10].

Another peaks that might be of interest occur around $250\text{--}300\text{ cm}^{-1}$ which can be assigned to both TeO_3 tp and Er–O bond [16]. As this peaks become increasingly sharper it can be said that the TeO_3 tp structural unit increases as the Er_2O_3 content increases. This argument is in agreement as has been reported elsewhere [16]. Thus it can be said that Er^{3+} in the glass may significantly modified the Te–O networking structure.

5. Conclusions

In the present work, tellurite glasses of $(80 - x)\text{TeO}_2\text{--}20\text{ZnO--}(x)\text{Er}_2\text{O}_3$ system ($0.5\text{ mol}\% \leq x \leq 2.5\text{ mol}\%$) has successfully been made by melt-quenching technique. The DTA and Raman spectra of glass system have successfully been studied. From the results above discussion, some conclusions may be made:

- (i) A stable and wide glass formation range can be obtained in the $(80 - x)\text{TeO}_2\text{--}20\text{ZnO--}(x)\text{Er}_2\text{O}_3$ system ($0.5\text{ mol}\% \leq x \leq 2.5\text{ mol}\%$).
- (ii) As the Er_2O_3 content increases, the Raman peaks intensity around $640\text{--}670\text{ cm}^{-1}$ decreases while the peaks intensity around $720\text{--}740\text{ cm}^{-1}$ increases.
- (iii) The decreases or/ and the increases of the Raman peaks intensity is might be due to the conversion of glass network from TeO_4 tbp units to TeO_3 tp units.

Acknowledgements

The authors wish to thank the Ministry of Science, Technology and Innovation for their financial support un-

der Vot 74532. We would also thanks to UTM for there continue support on this project.

References

- [1] Gan Fuxi, Laser Material, Word Scientific Publishing Co. Pvt. Ltd, 1995.
- [2] A. Nukui, T. Taniguchi, M. Miyata, J. Non-Cryst. Solids 293–295 (2001) 255.
- [3] R. El-Mallawany, Tellurite Glasses Handbook: Physical Properties and Data, CRC Press LLC, 2002.
- [4] D.L. Sidebottom, M.A. Hruschka, B.G. Potter, R.K. Brow, J. Non-Cryst. Solids 222 (1997) 282.
- [5] S. Marjanovic, J. Toulouse, H. Jain, C. Sandmann, V. Dierolf, A.R. Kortan, N. Kopylov, R.G. Ahrens, J. Non-Cryst. Solids 322 (2003) 311.
- [6] L.L. Neindre, S. Jiang, B.C. Hwan, T. Luo, J. Watson, N. Peyghambarian, J. Non-Cryst. Solids 255 (1999) 97.
- [7] H. Burger, K. Kneipp, H. Hobert, W. Vogel, J. Non-Cryst. Solids 151 (1992) 134.
- [8] P. Charton, P. Thomas, P. Armand, J. Non-Cryst. Solids 321 (2003) 81.
- [9] A. Abd El-Moneim, Mater. Chem. Phys. 73 (2002) 318.
- [10] V. Nazabal, S. Todoroki, A. Nukui, T. Matsumoto, S. Suehara, T. Hondo, T. Araki, S. Inoue, C. Rivero, T. Cardinal, J. Non-Cryst. Solids 325 (2003) 85.
- [11] M.R. Sahar, N. Noordin, J. Non-Cryst. Solids 184 (1995) 137.
- [12] M.R. Sahar, A.K. Jehbu, M.M. Karim, J. Non-Cryst. Solids 213 & 214 (1997) 164.
- [13] S. Kawasaki, T. Honma, Y. Benino, T. Pujiwara, R. Sato, T. Komatsu, J. Non-Cryst. Solids 325 (2003) 61.
- [14] H. Li, Y. Su, S.K. Sundaram, J. Non-Cryst. Solids 293–295 (2001) 402.
- [15] J.C. Sabadel Armand, D. Cachau-Herreillat, P. Baldeck, O. Doctot, A. Ibanez, E. Philippot, J. Solid State Chem. 132 (1997) 411.
- [16] T. Komatsu, H. Tawarayama, H. Mohri, K. Matusita, J. Non-Cryst. Solids 135 (1991) 105.
- [17] L. Hu, Z. Jiang, Phys. Chem. Glasses 37 (1) (1996) 19.