Synthesis and Optical Characterization of Nd^{3+} doped TeO_2-PbO-Li_2O

M. R. Sahar, A. Kassim and R. Arifin.
Advanced Optical Materials Research Group (AOMRG), University Teknologi Malaysia,
81310 UTM, Skudai, Johor, MALAYSIA.

Abstract

Glass based on Nd^{3+}-doped TeO_2-PbO-Li_2O has successfully been made by melt quenching technique and their thermal parameters have been determined using Differential Thermal Analyzer (DTA). The glass is then nucleated and/or growth by controlled heat treatment at slightly below the crystallization temperature. The X-ray diffraction (XRD) technique is used to estimate the nano-crystallite size. Meanwhile, the optical characterization has been determined using the Photoluminescence Spectroscopy. It is found out that the crystallite size is about 20 nm and very much depending on the heat-treatment time. Meanwhile, the intensity of the luminescence spectra is very much depending on the concentration of the dopant.

Keyword: tellurium glasses, melt quenching technique, optical characterization

Introduction

Nano-structured glasses are transparent materials containing nano-sized crystals inside the amorphous matrix. They are important for laser technology since they are potentially not as expensive as a crystal. They can be tailored to have compromise properties between pure ceramics and glass. In term of fabrication viewpoint, they are relatively much easier and faster to prepare than those of laser crystal. They also have wide applications for active and passive optical applications, solar collectors, up-conversion devices, laser active and passive media, photonic devices and many other [1−4]. It has been reported that the nano-glass exhibits higher ductility and hardness and enhanced fluorescence behavior [5]. Nano-structured glass has previously been developed by crystallization of amorphous using controlled heat treatment temperature and time [6]. By this way, a crystallite of about few nanometers in size, distributed throughout the glass matrix can be obtained.

Tellurite glass is of interest due to their low phonon absorption, thus giving maximum electronic up-conversion which is needed to be a laser source [7]. Doping with larger rare earth ions concentration is therefore needed to increase the pumping absorption in a short cavity length [8]. This method has been further used by Santa-Cruz et al [9] to produce a glass system in which the local crystal field environment of the rare earth ions is the same as in the crystalline form. However, the formation of grain boundary may reduce the homogeneity of the glass thus producing some losses during pumping process.

Experimental

The Nd^{3+}-doped tellurite glass of TeO_2-PbO-Li_2O-Nd_2O_3 glass system was prepared by melt-quenching technique. Batches of 20 g were prepared from certified reagent grades of TeO_2 (99.95% purity), Li_2CO_3 (97% purity), PbO (98% purity) and Nd_2O_3 (99.995% purity). The chemicals were firstly mixed thoroughly in a platinum crucible before being heated at 1000 ^{o}C for half an hour. After the batch was completely melted, the melts was cast onto the preheated stainless steel plate followed by annealing at 300 ^{o}C for 5 hours before allowed to cool down to room temperature. The glass sample is then cut and polish at the thickness of about 2.0 mm. Pyris Diamond TG/DTA (Thermogravimetri/Differential Thermal Analyzer) was used to determine the thermal characteristics of the glasses. In this case, 10 mg of glass samples are heated in the TG/DTA furnace with a heating rate of 10°C/min from 25°C to 1000°C.

For the heat treated experiment, the glass samples is put in a furnace to a temperature slightly below glass crystallization temperature, T_c, (at 420°C for 60 min) to promote a crystal growth in the bulk glass. X-ray diffraction technique is used to determine the crystallinity

of the non-heat treated samples and to identify the phase of the crystals precipitated in the glass matrix using Phillips Analytical X-ray Diffractometer, operated at 30 kV and 20 mA using a CuK_α source with $\lambda = 0.15418$ nm. The luminescence spectra are also measured in the region of 600 nm to 1200 nm at room temperature by using Nanosecond Luminescence Spectroscopy System, Model NT340/1 Ekspla. The emission spectra were obtained by exciting laser from tunable Nd: YAG laser system NT342. The luminescence signal was monitor by monochromator SP2300 equipped with photomultiplier in the photon counting mode and recorded under data acquisition unit (DAQ).

Results

Table 1 shows the T_c and T_g for the glasses. From Table 1, it can be seen that T_g increases as the Nd_2O_3 content is increased which indicates the changes in structural network [7]. The result also shows that T_c increases which implies that the glass tend to be crystallized easily. This is the reason why the sample containing maximum Nd_2O_3 content has been chosen to be crystallized. Other workers

have also shown that the nucleation can be seen when the sample is annealed around transformation temperature T_g [5]. A narrow sharp peak indicates that the nucleation and/or growth occur during annealing.

Fig. 1 shows the XRD patterns for the non-heat and heat treated samples, both containing 2.5 mol% Nd_2O_3. From Fig 1, it can be seen that the non-heat treated samples shows an amorphous behavior while for the heat treated samples the existence of some peaks can be observed. This result indicates that some crystals are starting to growth.
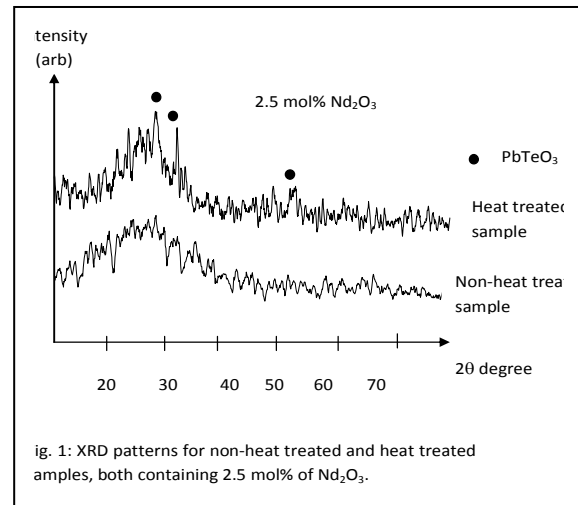

ig. 1: XRD patterns for non-heat treated and heat treated amples, both containing 2.5 mol% of Nd_2O_3.

Table 1: The T_c and T_g for some Nd-doped tellurite glasses

Nd_2O_3 (mol%)	0	0.5	1.0	1.5	2.0	2.5
T_g (°C)	293	300	305	310	315	320
T_c (°C)	370	390	400	405	415	430

Fig. 2 shows the emission spectrum of the Nd^{3+} doped tellurite glass under excitation at 585 nm. From the results, six significant emission peaks are observed around 485 nm, 560 nm, 605 nm, 880 nm, 1062 nm and 1340 nm which correspond to the $^4G_{11/2} \rightarrow ^4I_{11/2}$, $^4G_{11/2} \rightarrow ^4I_{13/2}$, $^4G_{11/2} \rightarrow ^4I_{15/2}$, $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$, $^4F_{3/2} \rightarrow ^4I_{13/2}$ transition respectively. The emission spectrum shown in Fig. 2 represented the rest of the Nd^{3+} doped tellurite glasses emission spectra. For the near infrared spectral region, three significant spontaneous transitions probability peaks were observed with a transition from $^4F_{3/2} \rightarrow ^4I_{11/2}$ is found to be dominant than the other two transitions in this region. It shows no significant changes in emission spectral peaks as the Nd^{3+} incorporated into the glass system with different mol percentages.
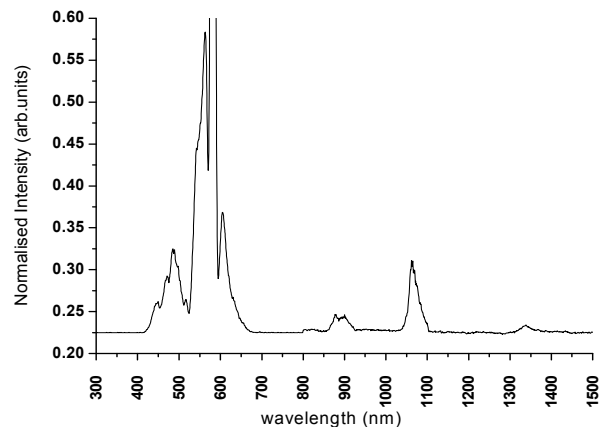

Fig. 2: A typical emission spectrum of the TeO_2-PbO-Li_2O-Nd_2O_3 glass under excitation at 585 nm.

Discussion

All peaks as appears in Fig.1 for heat treated samples are assigned for $PbTeO_3$ phase. There of course some other minor peaks which can be seen starting to grow and perhaps belong to other crystal phase. However, these peaks are outside the limit for x-ray to detect clearly. Using the Scherrer formula, the average crystal size (d) can be measured using [10],

$$d = \frac{k\lambda}{\beta \cos\theta}$$

where $k = 0.9$ (approximately), λ is the wavelength of the radiation used (0.1541 nm for CuK_α), β the full width at half maximum and θ is the Bragg angle. Thermal treatment at 420^oC at 60 min led to mean crystallite size of about 20 nm. The size would be expected to increase if longer time for heat treatment is applied. This should be in accordance with the crystal growth equation given by Hillig. Further investigation showed that the nano-crystal is belonging to α-TeO_2 phase which provides the low phonon energy environment for the rare earth ions [11].

For the emission spectra, the peak is dominant at 560 nm (green emission) which is due to $^4G_{11/2} \rightarrow {}^4I_{15/2}$ transition while for red emission at ~605 nm, the transition is due to $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. Chao Liu *et al*. [12] have shown that for nano-structured glass, the peak intensity is very much higher compare to the parent glass. It means that by controlling the crystallite size, the intensity of each peak can be controlled using the suitable concentration of the dopant. This would suggest that the multi-colour can potentially be generated by the rare-earth doped nano-glass. Another report also shows that the lifetime decay curve for higher rare earth concentration is no more in exponential trend as might be expected, instead, the effective decay time should be calculated using the equation suggested by Nakazawa [13]. Generally, the Nd^{3+} ions can be located either in the glass matrix, inside the nano-crystal or at the interface between the crystallite and the glassy phase. In this case, it is less possible that the Nd^{3+} ions would enter the crystal site since Pb ions are relative quite heavy.

Conclusion

The Nd^{3+} ions can be located either in the glass matrix, inside the nano-crystal or at the interface between the crystallite and the glassy phase. It is less possible that the Nd^{3+} ions would enters the crystal site since Pb ions are relative quite heavy.

Acknowledgement

References

[1] K. Tanaka, T. Mukai, T. Ishihara, K. Hirao, N. Soga, S. Soga, M. Ashida, R. Kato., *J. Am. Ceram. Soc*. **76** (1993) 2839.

[2] G.H. Beall, L.R. Pinckney., *J. Am. Ceram. Soc*. **82** (1999) 5.

[3] M.F. Joubert., *Opt. Mater*. **11** (1999) 181.

[4] L. F. Johnson, H. Guggenheim., *Appl. Phys. Lett*. **19** (1971) 44.

[5] D.R. MacFarlane, J.S. Javorniczky, P.J. Newman, D.J. Booth, *J. Non-Cryst. Solids*. **256 & 257** (1999) 366.

[6] D.H. Ping, D.X. Li, H.Q. Ye, *J. Mater*. Sci. Lett. 14 (1995) 1536.

[7] 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.

[8] V.K. Bogdanov, W.E.K. Gibbs, D.J. Booth, J.S. Javorniczky, P.J. Newman, D.R. MacFarlane, *Opt. Commun*. **132** (1996) 7376.

[9] P. Santa-Cruz, D. Morin, J. Dexpert-Ghys, A. Sadoc, F. Glas, F. Auzel, *J. Non-Cryst. Solids*. **190** (1995) 238.

[10] B.D. Cullity, Elements of X-ray Diffraction, 2nd ed., Addison-Wesley, Boston, Massachusetts, (1978).

[11] Y. Wang, J. Ohwaki,. *Appl. Phys. Lett*. **63** (1993) 3268.

[12] C. Liu, J. Heo, *J. Non-Cryst. Solids*. **352** (2006) 5325.

[13] E. Nakazawa, in: S. Shionoya, W.M. Yen(Eds.), Phosphor Hand-book, CRC Press, Boca Raton, (1999) 101