Solid State Phenomena
ISSN: 1662-9779, Vols. 181-182, pp 383-387
doi:10.4028/www.scientific.net/SSP.181-182.383

Online: 2011-11-15

Effects of Chloride Ion in TeO_2-ZnO-$ZnCl_2$-Li_2O-Eu_2O_3 Glass System

M. R. Sahar[a], R. Arifin and S. K. Ghoshal

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

[a]mrahim057@gmail.com

Keywords: TeO_2 - ZnO - $ZnCl_2$ - Li_2O - Eu_2O_3 glass system; Absorption spectra; Judd-Ofelt analysis; Quality factor; Radiative lifetime

Abstract. A series of zinc oxychloride tellurite glass based on (79 – z) TeO_2 - 10ZnO - (z) $ZnCl_2$ - 10Li_2O - 1Eu_2O_3 (where z = 0, 10, 20, 25 and 30 mol %) are successfully prepared by the melt quenching method. The optical properties are characterized by means of Raman spectra, UV-Vis and photoluminescence spectroscopy. It is found that the Raman spectrum of the glass shows three main peaks in the vibrational band in the vicinity of 430, 670 and 770 cm^{-1}. The intensity of all bands is decreased as the $ZnCl_2$ contents are increased from 0 to 30 mol % but the intensity ratio (I_{770} / I_{670}) increased. This may arise from the change in the structural chains from TeO_4 to TeO_{3+1} or to a TeO_3 polyhedron shape. Using the UV-Vis absorption spectrum, the Judd-Ofelt (J-O) analysis is performed to determine the J-O parameters (Ω_2, Ω_4, Ω_6) and it is found that $\Omega_2 > \Omega_4 > \Omega_6$. The values of Ω_2, Ω_4 , Ω_6, the quality factor (Q) and the radiative lifetime (τ_{rad}) are found to increase with $ZnCl_2$ content up to 20 mol %. From photoluminescence spectrum, it is found that the value of the intensity ratio between $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transition increase with $ZnCl_2$ contents which illustrates that this glass can easily become laser material.

Introduction

Zinc tellurite glass is selected as one of the new optical materials since it has many advantages such as high refractive index (1.8 < n < 2.3), good chemical durability, high thermal expansion coefficient (more than 250 x 10^{-7} C^{-1}), high thermal stability, low glass transition temperature and high IR transmission from the ultra violet region to mid-infrared (0.33 - 6.5 μm) [1, 2, 3]. Zinc tellurite glass represents something of a compromise between the requirement for both a low phonons energy environment to minimize nonradiative losses as well as possessing good mechanical and optical properties. These advantages could make zinc tellurite glass a potential host material for rare earth ions dopant for laser applications [4, 5]. Due to the low molecular vibrational frequency the nonradiative relaxation of the tellurite glass tend to be inefficient [6]. However, there are not many studies about the effect of chloride ions on these glasses. Thus, the aim of this paper is to investigate the optical and spectroscopic properties of the TeO_2-ZnO-$ZnCl_2$-Li_2O glass doped with Eu^{3+} as a function of $ZnCl_2$ content. Intensity parameters, radiative lifetime and branching ratio are determined from the absorption spectra by using Judd-Ofelt theory.

Experimental

A series of glass samples, (79 – z)TeO_2 - 10ZnO – (z)$ZnCl_2$ - 10Li_2O - 1Eu_2O_3 where z = 0, 10, 20, 25, 30 mol % are prepared by melting mixtures of high-purity TeO_2, ZnO, $ZnCl_2$, Li_2CO_3 and Eu_2O_3 in a platinum crucible. The mixture is heated in an electrical furnace at a temperature 850^o C for 30 minutes. To ensure proper mixing and homogeneity, the molten liquid was shaken frequently and vigorously. After achieving the required viscosity, the melt is casted by pouring into a preheated stainless steel mould to quench to form glass. The amorphous nature of these samples is confirmed by X-ray diffraction technique using Bruker axs D5005 X-ray Diffractometer. For optical measurement, the annealed glass plates are well polished on both sides to a dimension of 20 mm x 20 mm x 2 mm. The optical absorption and emission spectra of the glass are recorded using Jenway 6505 UV-Vis Spectrophotometer and Perkin-Elmer Instruments LS 55 Luminescence Spectrometer, respectively.

Results and Discussion

From Figure 1, it is clear that the Raman spectrum shows a broad band around 440 cm^{-1} and two narrow modes around 670 cm^{-1} and 770 cm^{-1}. It is also observed that the intensity of the band at around 440 cm^{-1} is decreased with $ZnCl_2$ content. This shows that the Te-O-Te bonding is decreased as $ZnCl_2$ content increases. It is also observed that the intensity of both bands around 670 cm^{-1} and 770 cm^{-1} are decreased but the intensity ratio (I_{770} / I_{670}) is increased with $ZnCl_2$. This again shows that some of the bonding structures are changed from TeO_4 to TeO_{3+1} or TeO_3 polyhedral. The existence of TeO_{3+1} is confirmed as depicted in Figure 1. The higher intensity of the peak indicates that the bonding force constant is lower thus the network structure becomes more open [7]. The changes from TeO_{3+1} to TeO_3 with an increase in $ZnCl_2$ can be seen at the transition of the 734 cm^{-1} peak towards a higher energy. When the $ZnCl_2$ content is increased from 0 to 30 mol %, the peak shifts from 734 cm^{-1} to 779 cm^{-1} with a maximum phonon energy increased from 0.9125 eV (734 cm^{-1}) to 0.9680 eV (779 cm^{-1}). From Figure 1, it is also seen that the band intensity around 770 cm^{-1} decreases for $ZnCl_2$ content exceeding 20 mol %.

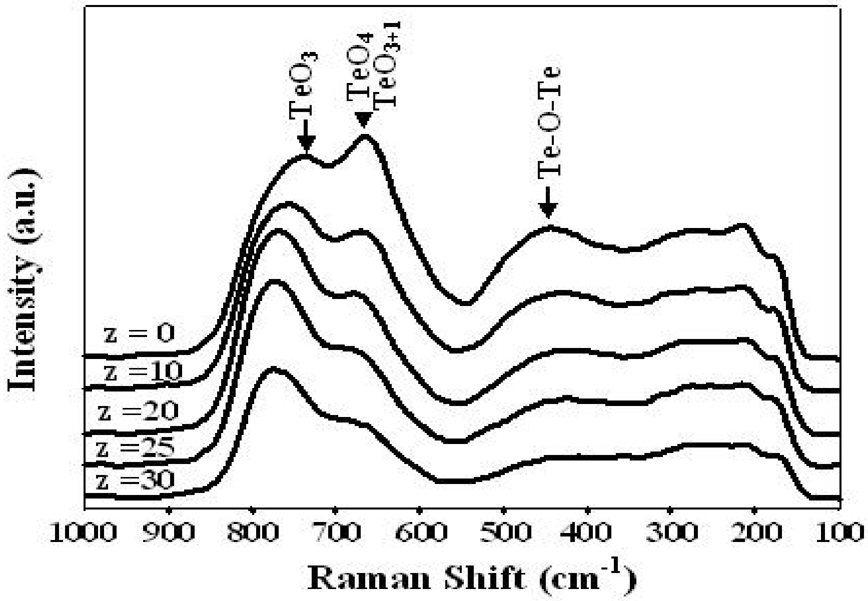

Fig. 1. Raman spectrum of (79 – z)TeO_2 - 10ZnO - (z)$ZnCl_2$ - 10Li_2O - 1Eu_2O_3 glass system, where z = 0, 10, 20, 25 and 30 mol %.

The absorption spectra of the samples with various $ZnCl_2$ content are shown in Figure 2. It can be seen that the transitions $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ occur in all sample, but for transition $^7F_0 \rightarrow {}^5D_4$ and $^7F_0 \rightarrow {}^5G_2$ can only be observed clearly for $ZnCl_2$ concentration more than 10 mol %. The increase in $ZnCl_2$ leads to a shift of the UV cut off to shorter wavelengths. In Figure 2, the absorption edge of rare-earth Eu_2O_3 doped glass occurs in the near-UV region. The optical absorption edge becomes more prominent as Eu_2O_3 is incorporated into the glass. The J-O parameters for various $ZnCl_2$ content are derived using least-squares fitting approach between the measured (P_{mea}) and calculated (P_{cal}) oscillator strength. The values for the optical spectroscopic ratio or spectroscopic quality factor $Q = \Omega_4 / \Omega_6$ introduced by Jacobs and Weber [8] is also calculated. All J-O parameters show an increase with $ZnCl_2$ concentration from namely, Ω_2, from 1.270 x 10^{-19} to 1.517 x 10^{-19} cm^2, Ω_4, from 0.244 x 10^{-19} to 0.581 x 10^{-19} cm^2 and Ω_6, from 0.118 x 10^{-19} to 0.138 x 10^{-19} cm^2 respectively with the increase of $ZnCl_2$ content from 0 mol % to 30 mol %. The trend for the Ω parameters in the glass system follows $\Omega_2 > \Omega_4 > \Omega_6$. It is well known that the parameter Ω_2, exhibits the dependence on the covalency between rare earth ions and ligands anions, since Ω_2 reflect the asymmetry of the local environment at the Eu^{3+} ion site. The higher the value of Ω_2 the less centro-symmetric the ion site is and less ionic its chemical bond with the ligands [9]. The slight increase of Ω_2 with an increasing of $ZnCl_2$ concentration in the glass system could indicate the increase of covalent character because of the different site occupancy of the ions on average [10].

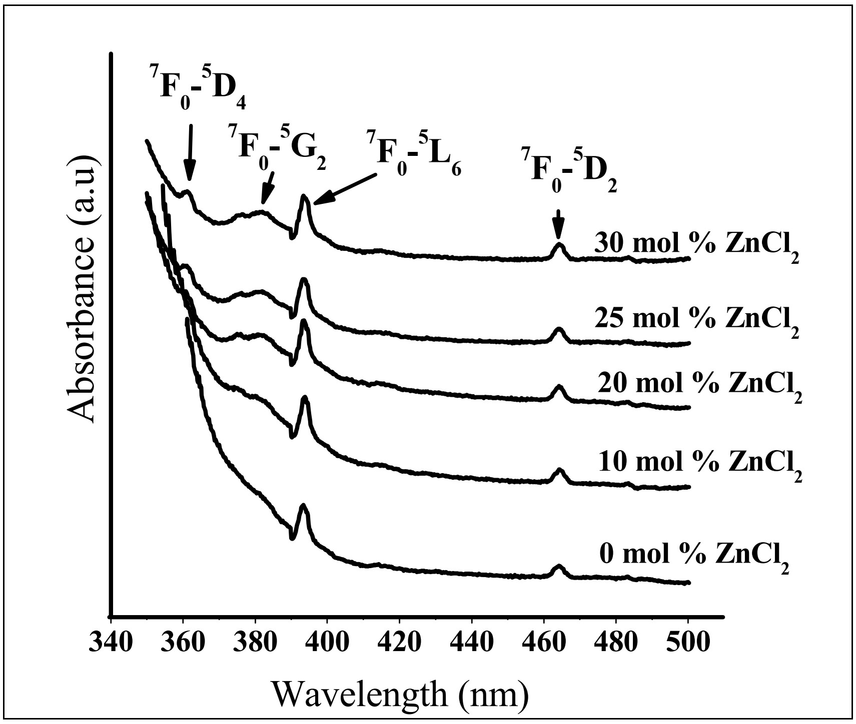

Fig. 2. Absorption spectrum of Eu^{3+} in the (79 – z)TeO_2 - 10ZnO - z$ZnCl_2$ -10Li_2O - 1Eu_2O_3 glass system, where z = 0, 10, 20, 25 and 30 mol %.

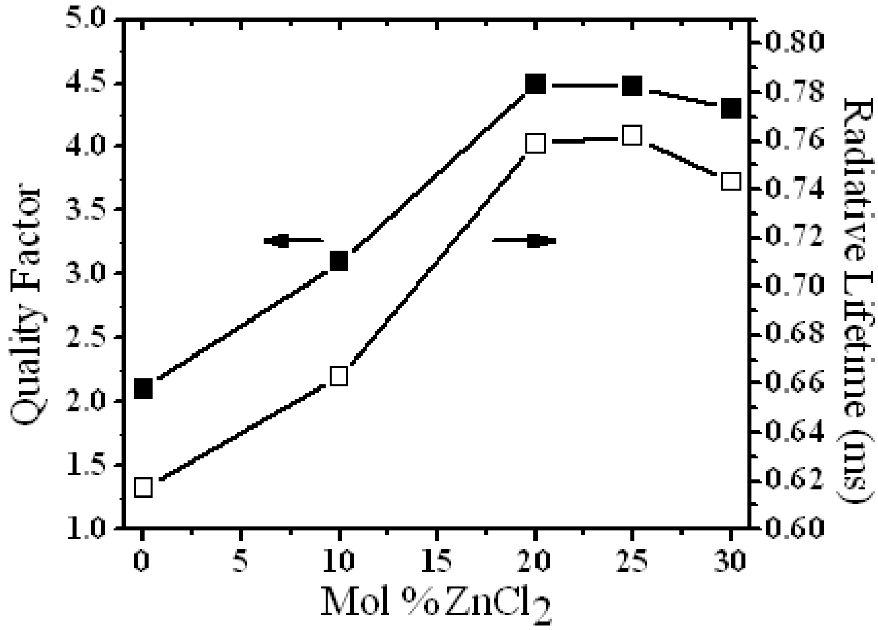

Fig. 3. Spectroscopic quality factor (Q) and radiative lifetime (τ_{rad}) of the $^5D_0$ level as a function of $ZnCl_2$ concentration.

Figure 3 shows the dependence of Q as a function of $ZnCl_2$ concentration. The value of Q increases from 2.067 to 4.495 for 20 mol % $ZnCl_2$ and then decreases to 4.210 for 30 mol % $ZnCl_2$. It indicates that the higher the value of Q, the better the optical glass and hence the stronger the laser $^5D_0 \rightarrow {}^7F_2$ transitions. On the other hand, the efficiency of $^5D_0 \rightarrow {}^7F_1$ transition is reduced [11, 12]. The τ_{rad} increases substantially with the introduction of zinc chloride into the tellurite matrix as shown in Figure 3. The τ_{rad} increased from 0.617 ms to 0.759 ms when 20 mol % $ZnCl_2$ are introduced into the tellurite matrix. The τ_{rad} is also desired to be as long as possible in order to permit a greater pulsed power. For higher $ZnCl_2$ content, τ_{rad} decreased from 0.759 to 0.743 ms for 30 mol % $ZnCl_2$. This change clearly shows a maximum at about 20 mol % of $ZnCl_2$, as obtained as maximum in τ_{rad}. This is the evidence that halide $ZnCl_2$ does modifies the local electrostatic field symmetry of the rare earth ion Eu^{3+} and can produce a substantial increase of the intrinsic radiative lifetime. The chloride ion Cl^- may be replaced by an oxygen ion somewhere in coordination sphere and disturbing the local electron density so the electrostatic environment of rare earth ion was altered.

The OH content of this glass also decreased with zinc chloride as shown from the FTIR spectra, suggesting that this compound may react with the OH group, probably giving zinc oxide and HCl [13]. This dehydration effect may explain the fact that the fluorescence intensities and lifetimes appear to reach a maximum for 20 mol% $ZnCl_2$ after which it may leads to an increase in ion-ion interactions, clustering and nonradiative decay from $^7F_6$ to ground $^7F_0$ along with multi-phonon relaxation, which responsible for the subsequent decrease of the lifetimes.

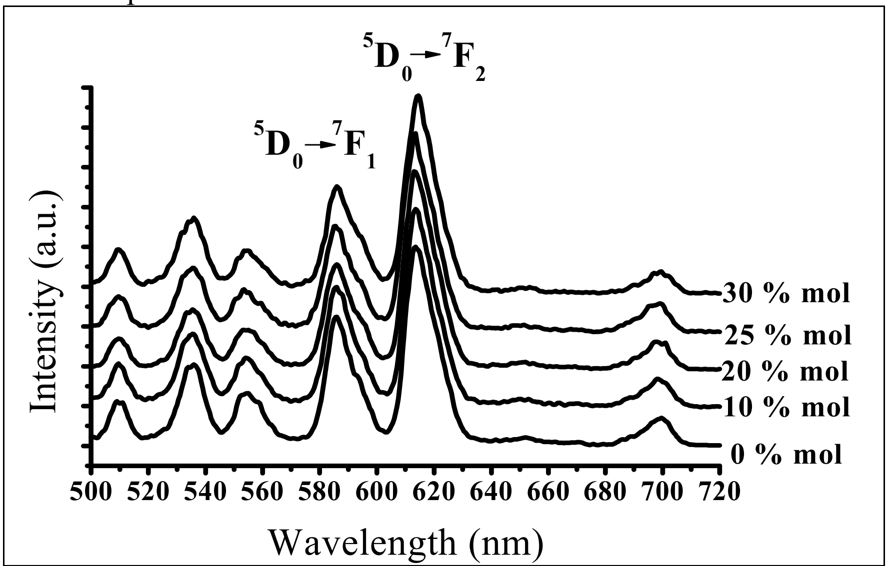

Fig. 4. Emission spectrum of Eu^{3+} in the glass samples with different $ZnCl_2$ content at 397 nm excitation.

Figure 4 represents the emission spectrum of Eu^{3+} in the glass with various $ZnCl_2$ contents. From Figure 4, it can be observed that all the glass samples showed maximum emission intensity at 613 nm and similar full width half maximum (FWHM) value. For wavelength less than 600 nm, the addition of $ZnCl_2$ decreased the intensity of the blue and green emission. The value of the intensity ratio of ($^5D_0 \rightarrow {}^7F_2$) / ($^5D_0 \rightarrow {}^7F_1$) is increased from 1.54 to 1.87 for 0 to 20 mol % $ZnCl_2$ and continued to decrease to 1.84 when the $ZnCl_2$ content is increased to 30 mol %. The increase in the value of the intensity ratio can be justified by making an assumption that the Eu^{3+} ions has the tendency to be in a less symmetrical configuration [14, 15]. The addition of $ZnCl_2$ exceeding 20 mol % cause the glass structure to become less rigid and as such the local structure of ions become less distorted [16, 17]. The increase in the value of intensity ratio of ($^5D_0 \rightarrow {}^7F_2$) / ($^5D_0 \rightarrow {}^7F_1$) implies that the Eu^{3+} dopant has high tendency to be an active laser material in the glass.

Summary

The optical properties of zinc oxychloride tellurite glass with varying $ZnCl_2$ contents prepared by melt quenching technique are studied employing spectroscopic methods. The role of $ZnCl_2$ on the structural and optical properties is examined in detail. The J-O parameters are calculated to complement the experimental observations. The addition of $ZnCl_2$ is caused an additional change in the bonding structure of the glass from TeO_4 to TeO_{3+1} or TeO_3 polyhedral where the network structure became more open. The band shift in the absorption spectrum is also increased and the UV intercept at a point less than 360 nm. The value of J-O parameters (Ω_2, Ω_4, Ω_6), the spectroscopic quality factor (Q), the radiative lifetime (τ_{rad}) are also increased with $ZnCl_2$ content. The increase in the Q value and τ_{rad} are due to the dehydration effect where the OH content in the glass system decreased. The increase in the Q value showed better optical properties for glass which gave rise to a high value of the intensity ratio for the $^5D_0 \rightarrow {}^7F_2$ / $^5D_0 \rightarrow {}^7F_1$ transitions.

Acknowledgements

The authors gratefully acknowledge the financial support from Universiti Teknologi Malaysia through the research grants from MOSTI (Vot. 78409) and GUP (Vot.Q.J.13000.7126.00J76).

References

[1] D. L. Sidebottom, M. A. Hruschka, B. G. Potter and R. K. Brow: J. Non-Cryst. Solids Vol. 222 (1977), p. 282.

[2] J. S. Wang, E. M. Vogel and E. Snitzer: Opt. Mater. Vol. 3 (1994), p. 187.

[3] H. Nahu, T, Uchigaki, K, Kamiya, H. Kanbara and K. Kubodera: Jpn. J. Appl. Phys. Vol. 31 (1992), p. 3899.

[4] R. Sakai, Y. Benino and T. Komatsu: Appl. Phys. Lett. Vol. 77 (2000), p. 2118.

[5] E. R. Taylor, L. N. Ng, N. P. Sessions and H. Buerger: J. Appl. Phys. Vol. 92 (2002), p. 112.

[6] V. Nazabal, S. Todoroki, A. Nukui, T. Matsumoto, S. Suehara, T. Hondo, T. Araki, S. Inoue, C. Rivero and T. Cardinal: J. Non-Cryst. Solids Vol. 325 (2003), p. 85.

[7] A. A. El-Moneim: Materials Chemistry and Phys. Vol. 73 (2002), p. 318.

[8] R. R. Jacobs and M. J. Weber: IEEE. J. Quantum Electron. Vol. 12 (1976), p. 102.

[9] C. K. Jorgensen and R. Reisfeld: J. Less-Common Met. Vol. 93 (1983), p. 107.

[10] P. Subbalakshmi and N. Veeraiah: J. Phys. and Chem. Solids Vol. 64 (2003), p. 1027.

[11] B. Viana, M. Palazzi and O. Le Fol: J. Non-Cryst. Solids Vol. 215 (1997), p. 96.

[12] M. Ajroud, M. Haouari, H. Ben Ouada, H. Maaref, A. Brenier and C. Garapon: J. Phys. Vol. 12 (2000), p. 3181.

[13] B. Bridge, T. E. Bavins, D. Woods and T. Woolven: Non-Cryst. Solids Vol. 88 (1986), p. 262.

[14] R. Reisfeld: Structure and Bonding. Vol. 13 (1973), p. 53.

[15] R. K. Brow, D. R. Tallant and G. L. Turner: J. Amer. Ceramic Soc. Vol. 79 (1996), p. 2410.

[16] D. Lery, R. Reisfeld and D. Avnir: Chem. Phys. Lett. Vol. 109 (1984), p. 593.

[17] M. Ferrari, R. Campostrini, G. Carturan and M. Montagna: Phil. Mag. B. Vol. 65 (1992), p. 251.