

## The Structural Properties of Trivalent Rare Earth Ions (Er<sup>3+</sup>) Doped Borotellurite Glass

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### Article history

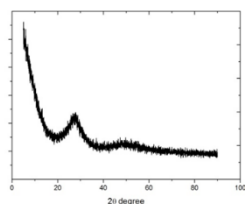
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### Graphical abstract



### Abstract

Six samples of borotellurite glasses with system (80-x)TeO<sub>2</sub>- 10B<sub>2</sub>O<sub>3</sub> - 10PbO - xEr<sub>2</sub>O<sub>3</sub> (x=0.0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%) have been prepared by using the conventional melt-quenching method. Some basic physical parameters such as density and molar volume were measured. The result reveals that the density and molar volume increases with the increases of mol% of Er<sub>2</sub>O<sub>3</sub>. The amorphous nature of the glass has been characterized using X-ray Diffraction (XRD) and all glasses are found to be amorphous in nature. The structure was analysed by FTIR spectroscopy. The FTIR spectra were recorded at room temperature in the frequency range from 650 to 4000 cm<sup>-1</sup> using Attenuated Total Reflectance (ATR) method. From the IR results, the absorption bands were found to be in the range 667-669 cm<sup>-1</sup>, 710-712 cm<sup>-1</sup>, 880-887 cm<sup>-1</sup>, 981-997 cm<sup>-1</sup> and 1190-1204 cm<sup>-1</sup> which correspond to the stretching and bending vibrations mode. The absorption peaks around 1386-1388 cm<sup>-1</sup> and 3741-3748 cm<sup>-1</sup> which ascribed to the hydroxyl-metal bond and hydroxyl-hydrogen bond stretching vibration also have been observed. The FTIR results demonstrate that the existing of erbium in the composition leads to good structural properties thus creating potential for this glass in laser applications.

**Keywords:** Borotellurite glass; erbium; density; FTIR spectra

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### 1.0 INTRODUCTION

In recent years, the studies on trivalent rare earth ions doped host matrices have been increased due to their excellent potential applications in many optical devices such as upconversion lasers, sensors, telecommunications and display devices [1, 2]. Tellurium oxide (TeO<sub>2</sub>) based glasses are of scientific and technology interests due to their distinctive properties such as low melting temperatures, good mechanical stability, fine thermal and chemical durability, high refractive indices and good infrared transmission which creates possible application in photonic and optical devices [3-10]. Besides, Te O<sub>2</sub> glass is non-hygroscopic compared to phosphate and borate glasses [11].

It is well known that a pure TeO<sub>2</sub> does not become glass under usual melt-quenching method and the addition of other modifier such as alkali, alkaline earth and transition metal oxides are needed [12, 13]. The addition of alkali or alkaline earth modifiers into pure TeO<sub>2</sub> glass system will cause a change in tellurium coordination thus the incorporation of second oxide component is needed to ensure the stability of the glass structure [14, 15].

Meanwhile, borate glasses are the most suitable for the design of the new optical devices because of their good rare

earth ion solubility, high transparency, low melting point, high thermal stability and cost effective properties [16]. However, due to its higher phonon energy and difficulty to obtain high efficient infrared and upconversion visible emission, borate glass did not gain much interest [17].

By considering the compensation between borate and tellurite properties, the incorporation of B<sub>2</sub>O<sub>3</sub> into the TeO<sub>2</sub> host matrix is possible in order to enhance the glass stability and performance. Borotellurite glass represents favorable cooperation between the requirements of lower phonon energy and a relatively high thermal stability, high chemical durability as well as eases of fabrication [17]. In fact, the introduction of B<sub>2</sub>O<sub>3</sub> into TeO<sub>2</sub> host matrix is proposed in order to enhance glass quality due to their excellent properties.

Due to the interesting properties of Erbium doped borotellurite glass, therefore in this work a series of Er<sup>3+</sup> doped borotellurite glass were synthesized via melt-quenching technique. Their physical and structural properties will be studied and analyzed by means of their XRD, density, molar volume and FTIR spectra. The results are analysed and discussed with respect to mol% of Er<sup>3+</sup> content.

## 2.0 EXPERIMENTAL

The  $\text{Er}^{3+}$  doped borotellurite glasses with the chemical composition  $(80-x)\text{TeO}_2 - 10\text{B}_2\text{O}_3 - 10\text{PbO} - x\text{Er}_2\text{O}_3$  ( $x=0.0, 0.5, 1.0, 1.5, 2.0, 2.5$  mol%) were prepared by following the melt-quenching method. The total weight of element powders is 10 grams and is calculated in mol percent (mol %). For the mixing process, the batches underwent a milling process for about one hour in order to obtain homogeneous mixtures. The glass mixtures are then placed in a closed alumina crucible before being melted at an electric box furnace of temperatures  $1000^\circ\text{C}$  for 30 minutes.

The molten was air quenched by pouring it onto a preheated stainless-steel plate at  $400^\circ\text{C}$  that kept in another furnace. The molten should be poured out immediately in order to avoid solidification due to humidity. Then, the sample is subjected for annealing process at  $400^\circ\text{C}$  for five hours to relieve any residual stress and air bubbles which could cause embrittlement to the samples. At the end of annealing process, the furnace was switched off and the glass is allowed to cool down gradually to room temperature. The glass samples were then been polished on both sides for the measurement. The glasses obtained were transparent and in a good quality.

The density of the glass samples was measured by using Electronic densitometer at room temperature based on Archimedes principal with distilled water as the immersion liquid. The physical properties of  $\text{Er}^{3+}$  doped borotellurite glass are presented in Table 1.

The X-ray diffraction patterns of the prepared glass samples were recorded using X'Pert PRO Panalytical Diffractometer to confirm its amorphous nature. The FTIR spectral measurements were carried out using Perkin-Elmer Spectrum 400 FT-IR/ FT-NIR Spectrometer in the wave number range  $650\text{--}4000\text{ cm}^{-1}$  following Attenuated Total Reflectance (ATR) method in order to identify the functional groups of the  $\text{Er}^{3+}$  doped borotellurite glass. All these measurements were carried out at room temperature.

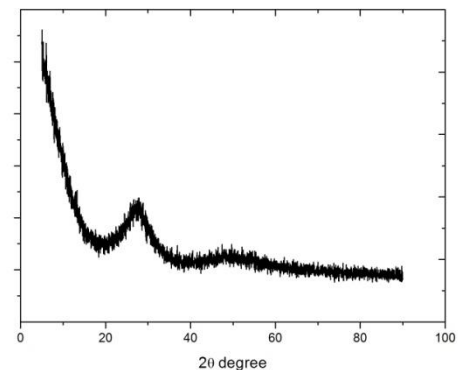
## 3.0 RESULTS AND DISCUSSION

Table 1 depicted physical properties of  $\text{Er}^{3+}$  doped borotellurite glass system. From Table 1, the results show a variant of colour as it changes from light orange to orange with respect to mol% of  $\text{Er}^{3+}$  content. As visualized, the glass samples obtained are in a good quality since they show no sign of devitrification. The glasses are also transparent and crystal clear.

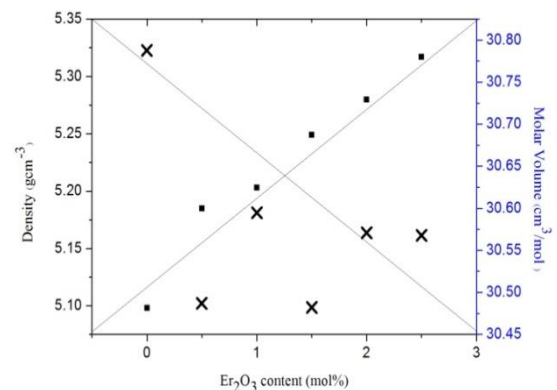
The XRD analysis is usually used as a definitive technique to identify unknown crystalline materials in an extensive range of materials especially where the individual particles are too small to be acknowledged by microscopic technique [18]. The XRD pattern of an amorphous is different from the crystalline material as amorphous shows no diffraction peaks. The X-ray diffraction patterns of the borotellurite glass system were recorded in the range  $5^\circ \leq 2\theta \leq 90^\circ$ . Consequently, Figure 1 presents typical XRD patterns of  $0.5\text{Er}^{3+}$  doped borotellurite glasses. From Figure 1, it could be seen that the patterns do not exhibit any diffraction line which confirms the amorphous nature of the glasses. Therefore, this sample can be classified as pure amorphous which shows a good agreement with previous research done elsewhere [18-20].

**Table 1** Physical properties of  $\text{Er}^{3+}$  doped borotellurite glass

| Glass Sample (mol % of $\text{Er}_2\text{O}_3$ ) | Remarks      | Density, $\rho$ ( $\text{gcm}^{-3}$ ) | Molecular Weight, M (g/mol) | Molar Volume, $V_m$ ( $\text{cm}^3/\text{mol}$ ) |
|--|--------------|---------------------------------------|-----------------------------|--|
| 0.00   | Light Orange | 5.098                                 | 156.959                     | 30.788   |
| 0.50   | Light Orange | 5.185                                 | 158.074                     | 30.487   |
| 1.00   | Light Orange | 5.228                                 | 159.188                     | 30.449   |
| 1.50   | Orange       | 5.249                                 | 160.303                     | 30.482   |
| 2.00   | Orange       | 5.280                                 | 161.417                     | 30.571   |
| 2.50   | Orange       | 5.317                                 | 162.532                     | 30.568   |



**Figure 1** A typical XRD pattern of  $\text{Er}^{3+}$  doped borotellurite glass

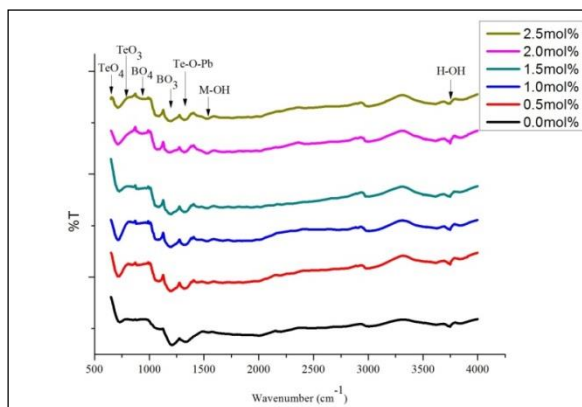


**Figure 2** Density and molar volume of  $\text{Er}^{3+}$  doped borotellurite glass

Meanwhile, Figure 2 shows the results of density and molar volume of the glass sample against  $\text{Er}_2\text{O}_3$  content. From Figure 2, the density shows a linear increment with respect to mol% of  $\text{Er}^{3+}$  doped borotellurite glass. The increase in density might be due to the incorporation of higher molecular masses of  $\text{Er}_2\text{O}_3$  ( $382.515\text{ g/mol}$ ) to replace the lower molecular mass of  $\text{TeO}_2$  ( $159.598\text{ g/mol}$ ). The incorporation of  $\text{Er}_2\text{O}_3$  into the glass system tends to change the Te atom coordination thus boosting the packing density of the glass structure. This result shows good agreement with previous research done elsewhere that the density of the glass samples increases with respect to  $\text{Er}^{3+}$  ions content [21]. The density of other tellurite based glasses has been analysed in a similar way [22-24].

However, in this work the molar volume show inversely trend of results to the density of the glass as shown in Figure 2. Similar trend of results were also been found by Saddek et al. in

their studies [25]. From Figure 2, it can be observed that the molar volume decreases slightly as the  $\text{Er}_2\text{O}_3$  content increases. However, as the Erbium content increases from 1.50 mol% to 2.5 mol%, the molar volume of the glass sample increases from  $30.482 \text{ cm}^3\text{mol}^{-1}$  to  $30.568 \text{ cm}^3\text{mol}^{-1}$ . An increasing of molar volume indicates an increasing of the interatomic distances due to the contribution of non-bridging oxygen thus reducing the glass compactness and their rigidity.



**Figure 3** Infrared Absorption Spectra of  $\text{Er}^{3+}$  doped borotellurite glass

Figure 3 shows the FTIR spectra of  $(80-x)\text{TeO}_2 - 10\text{B}_2\text{O}_3 - 10\text{PbO} - x\text{Er}_2\text{O}_3$  ( $0.0 \leq x \leq 2.5$  mol%) glass system in the frequency range from  $650 \text{ cm}^{-1}$  up to  $4000 \text{ cm}^{-1}$ . The IR bands are assigned based on the literature data on the wavenumber ranges that related to the corresponding vibrations of the structural units in various glassy systems. As can be seen in Figure 3, the absorption peaks position of these glasses has been summarized in Table 2.

**Table 2** IR Absorption peaks position of  $\text{Er}^{3+}$  doped borotellurite glass

| Sample (mol%) | IR Absorption peaks ( $\text{cm}^{-1}$ ) |     |     |     |      |      |      |
|---------------|--|-----|-----|-----|------|------|------|
| 0.0           | 667                                      | 725 | 880 | 981 | 1204 | 1386 | 3741 |
| 0.5           | 667                                      | 711 | 884 | 997 | 1191 | 1386 | 3748 |
| 1.0           | 667                                      | 714 | 884 | 997 | 1190 | 1388 | 3748 |
| 1.5           | 667                                      | 719 | 884 | 997 | 1197 | 1388 | 3748 |
| 2.0           | 667                                      | 710 | 887 | 997 | 1196 | 1388 | 3748 |
| 2.5           | 669                                      | 712 | 887 | 997 | 1190 | 1388 | 3744 |

Figure 3 shows seven significant IR absorptions region around  $667\text{-}669 \text{ cm}^{-1}$ ,  $710\text{-}725 \text{ cm}^{-1}$ ,  $880\text{-}887 \text{ cm}^{-1}$ ,  $981\text{-}997 \text{ cm}^{-1}$ ,  $1190\text{-}1204 \text{ cm}^{-1}$ ,  $1386\text{-}1388 \text{ cm}^{-1}$  and  $3741\text{-}3748 \text{ cm}^{-1}$ . From Figure 3, it is clearly been seen that the absorption band around  $667\text{-}669 \text{ cm}^{-1}$  are corresponding to  $\text{TeO}_4$  as reported [26]. The absorption band around  $710\text{-}712 \text{ cm}^{-1}$  could be assigned to  $\text{TeO}_3$  trigonal pyramid (tp) group. This is in agreement with the work done by [27].

Whereas, the absorption band at  $880\text{-}887 \text{ cm}^{-1}$  could be correspond to B–O stretching vibration of  $\text{BO}_4$  units while the absorption band around  $981\text{-}997 \text{ cm}^{-1}$  could be attributed to B–O bond stretching vibration of trigonal  $\text{BO}_3$  units as reported

[28]. Meanwhile, the absorption band at  $1190\text{-}1204 \text{ cm}^{-1}$  could be ascribed to the Te–O–Pb stretching vibrations. This result indicates that the existence of PbO in the glass network could create a structural change to the Te coordination polyhedron from  $\text{TeO}_4\text{tp}$  to  $\text{TeO}_3\text{tp}$  thus creating more non-bridging oxygen (NBOs). The absorption peak around  $1386\text{-}1388 \text{ cm}^{-1}$  are correspond to the hydroxyl-metal bond stretching vibration. Whereas, the absorption peak around  $3741\text{-}3748 \text{ cm}^{-1}$  region could be assigned to the hydroxyl-hydrogen bond stretching vibration. The existence of these hydroxyl group is very common to the oxide glass system [29]. These might be due to the entrapment of the water in the raw material from the ambient atmosphere. Kobayashi et al. identified the existence of  $\text{OH}^{-1}$  absorption bands due to the fundamental vibration for absorption bands around  $3400 \text{ cm}^{-1}$  [30].

#### 4.0 CONCLUSION

The present glasses  $(80-x)\text{TeO}_2 - 10\text{B}_2\text{O}_3 - 10\text{PbO} - x\text{Er}_2\text{O}_3$  ( $x=0.0,0.5,1.0,1.5,2.0, 2.5$  mol%) were prepared by melt-quenched technique. It is observed that the changes in density and molar volume with  $\text{Er}_2\text{O}_3$  content have been discussed in terms of ionic packing density and rigidity of the glass. From the IR results, the absorption bands are found to be in the range  $667\text{-}669 \text{ cm}^{-1}$ ,  $710\text{-}712 \text{ cm}^{-1}$ ,  $880\text{-}887 \text{ cm}^{-1}$ ,  $981\text{-}997 \text{ cm}^{-1}$  and  $1190\text{-}1204 \text{ cm}^{-1}$  which correspond to the stretching and bending vibrations mode.

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