

FOURIER TRANSFORM INFRARED SPECTROSCOPY AND OPTICAL PROPERTIES OF SAMARIUM DOPED ZINC BOROTELLURITE GLASSES

(Inframerah Transformasi Fourier dan Sifat Optik Kaca Samarium didop dengan Zink Borotelurit)

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Abstract

Zinc borotellurite glasses doped with Sm^{3+} ions of the $(70-x)\text{TeO}_2\text{-}20\text{B}_2\text{O}_3\text{-}10\text{ZnO-xSm}_2\text{O}_3$ system were prepared by a melt-quenching technique. The values of x varied from 0.0 mol% to 2.5 mol%. The studies on structural and optical characterisation of Sm^{3+} ions were carried out through Fourier transform infrared spectroscopy (FTIR), absorption spectra, optical band gap (E_{opt}) and Urbach energy (ΔE) analysis were presented for Sm^{3+} ions in zinc borotellurite glasses. From the FTIR analysis, the presence of BO_3 , BO_4 , TeO_3 , TeO_4 and B-O^- structural units in the prepared glasses was investigated. Three strong absorption peaks in the ultraviolet and visible regions were observed from absorption spectra due to transition between the ground state and various excited state of Sm^{3+} ions. The value of optical band gap, E_{opt} laid between 2.605 eV to 2.982 eV for the direct transition, and 2.768 eV to 3.198 eV for indirect transition, respectively. Meanwhile, the Urbach energy (ΔE) was observed in the range of 0.112 eV to 0.694 eV, respectively. Some other results were analysed and discussed in details.

Keywords: optical properties, zinc, borotellurite, absorption spectra

Abstrak

Kaca zink borotelurit didop dengan ion Sm^{3+} dalam sistem $(70-x)\text{TeO}_2\text{-}20\text{B}_2\text{O}_3\text{-}10\text{ZnO-xSm}_2\text{O}_3$ telah disediakan melalui kaedah konvensional sepuh lindap. Nilai x bervariasi dari 0.0 mol% hingga 2.5 mol%. Kajian terhadap pencirian struktur dan optik ion Sm^{3+} telah dilakukan melalui analisis spektroskopi inframerah transformasi Fourier (FTIR), spektrum penyerapan, jurang jalur optik (E_{opt}) dan tenaga Urbach (ΔE) telah dibentangkan untuk ion Sm^{3+} dalam kaca zink borotelurit. Dari analisis FTIR, kehadiran struktur unit BO_3 , BO_4 , TeO_3 , TeO_4 dan B-O^- dalam kaca yang disediakan telah dikaji. Tiga puncak penyerapan yang kuat pada ultraungu dan rantau terlihat telah diamati dari spektra penyerapan kerana transisi antara keadaan dasar dan pelbagai keadaan teruja ion Sm^{3+} . Nilai jurang jalur optik terletak antara 2,605 eV hingga 2,982 eV untuk transisi langsung dan 2,768 eV hingga 3,198 eV untuk transisi tidak langsung. Sementara itu, tenaga Urbach (ΔE) diperhatikan dalam lingkungan 0.112 eV hingga 0.694 eV, masing-masing. Beberapa keputusan lain telah dianalisis dan dibincang secara terperinci.

Kata kunci: sifat optik, zink, borotelurit, spektra penyerapan

Introduction

Rare earth (RE) ions incorporated with various glass oxides have attracted a great deal of interest due to their important role in the development of many optical devices, such as solid-state laser, light converters, sensor and optical communication fibres [1]. The RE ions doped in various glass hosts, such as zinc borotellurite [2], zinc tellurite [3], borotellurite [4] and zinc sodium phosphate [5] have received considerable attention. Amongst these glass hosts, zinc borotellurite glass systems are found suitable to be used as an excellent candidate for laser material due to their low phonon energy, high mechanical strength, high refractive index, large corrosion resistance, extended infrared transmittance (0.35 μm – 6.0 μm) and relatively high thermal stability [6,7]. Sailaja et al. reported that the RE ions, Sm^{3+} , can be used as a dopant in different glass hosts and crystal hosts for their high intense fluorescence in the visible region [8] since the absorption and emission spectra possess broad band region from ultraviolet to infrared [9]. This glass host is very interesting to analyse since the energy transfer process has relatively high quantum efficiency by means of their large energy gap (less non-radiative decay) between the lowest emitting level and next lower lying energy level. However, this glass also shows different quenching mechanisms [10].

In this paper, the effects of Sm^{3+} ions on the structural and optical properties of zinc borotellurite glass were investigated. This study is done to provide more data on the effect of Sm^{3+} ions on zinc borotellurite glass, which are suitable to be used for laser and optical devices. It is expected that the addition of Sm^{3+} ions in the glass network will enhance the optical properties of glass by lowering the optical band gap [11]. Their structural properties by means of FTIR spectroscopy, as well as their optical properties will be analysed and presented.

Materials and Methods

Sm^{3+} ions doped zinc borotellurite glasses with the chemical composition of $(70-x)\text{TeO}_2-20\text{B}_2\text{O}_3-10\text{ZnO}-x\text{Sm}_2\text{O}_3$ ($0.0 \leq x \leq 2.5$ mol%) were prepared by following the melt-quenching technique. Each batch had

chemical composition of about 10 g. The chemical compositions were firstly milled together for about 1 hour by using a milling machine to obtain homogeneous mixtures. Then, the mixtures were transferred into an alumina crucible and melted in an electric box furnace at 1000 $^\circ\text{C}$ for 30 min. The molten mixture was poured onto a stainless-steel plate, followed by an annealing process at 400 $^\circ\text{C}$ for 5 hours before it was allowed to cool down to room temperature gradually. Then, glass sample was polished before being used for any structural and optical studies.

The FTIR spectra of the glass samples were recorded by using Perkin - Elmer Spectrum 100 FT-IR Spectrometer system in the wavelength region 650–4000 cm^{-1} to identify the local structure and presence of fundamental functional groups. The absorption spectra were measured by using Perkin - Elmer Lambda 35 UV/VIS Spectroscopy in the range of 380-600 nm. By these absorption spectra, the optical absorption coefficient ($\alpha(\omega)$) can be calculated by using the equation as in [12]:

$$\alpha(\omega) = 2.303 \frac{A}{d} \quad (1)$$

where, A is the absorbance and d is the thickness of sample in cm^{-1} . The optical band gap, E_{opt} , of the glass samples can be calculated by using the known Mott – Davis equation [13]:

$$\alpha = \frac{B(\hbar\omega - E_{\text{opt}})^r}{\hbar\omega} \quad (2)$$

where, B is the band tailing parameter, E_{opt} is the optical band gap, $\hbar\omega$ is the incident photon energy while r is the index number used to decide the nature of the interband electronic transition causing the absorption ($r=1/2$ for direct allowed transition and $r=2$ for indirect allowed transition) [14]. Based on this equation, the graph of $(\alpha\hbar\omega)^2$ and $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ can be plotted and the value of optical band gap is the extrapolation of the linear region in these two graphs.

In addition, Urbach energy is another optical parameter that can be attained from the absorption spectra.

Referring to the equation from Urbach rule, it is obtained by calculating the reciprocal of slope in the graph of natural logarithm of $\alpha(\omega)$ as a function of photon energy, $\hbar\omega$:

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{\Delta E}\right) \quad (3)$$

where, α_0 is a constant and ΔE is the Urbach energy [15].

Results and Discussion

Figure 1 shows the FTIR spectra of zinc borotellurite glasses with respect to Sm^{3+} ions content. The spectra band around $714\text{-}735\text{ cm}^{-1}$ were assigned with the stretching vibrations of the Te-O bonds in trigonal bipyramid (TeO_4) with bridging oxygen and trigonal pyramid (TeO_3) with non-bridging oxygen (NBO) [16, 17]. The bands at $839\text{-}855\text{ cm}^{-1}$ and $1215\text{-}1218\text{ cm}^{-1}$ belonged to asymmetric stretching vibrations of B-O bonds in BO_4 tetrahedral and BO_3 trigonal units [18, 19]. Meanwhile, the peaks positioned at $1362\text{-}1367\text{ cm}^{-1}$ were due to the asymmetric stretching vibrations in trigonal BO_3 and trigonal B – O^- bond. Whereas the bands present at $2993\text{-}3003\text{ cm}^{-1}$ were attributed to the characteristic of the hydrogen bond in the glasses [20]. Finally, the absorption bands located around $3618\text{-}3748\text{ cm}^{-1}$ were due to fundamental stretching of molecular water groups, OH, as reported by Elbatal et al. [21].

Figure 2 shows the absorption intensity as a function of wavelength, normalised by the sample thickness of the glass with 0 mol% to 2.5 mol% Sm_2O_3 . These were three absorption peaks centred at 403 nm, 422 nm and 480 nm, that corresponded to the $^6\text{H}_{5/2} \rightarrow ^4\text{L}_{13/2}$, $^6\text{H}_{5/2} \rightarrow ^4\text{M}_{19/2}$ and $^6\text{H}_{5/2} \rightarrow ^4\text{I}_{11/2}$ transitions observed. Similar trend of results was also reported by Yaru et al., Som & Karmakar and Selvaraju & Marimuthu in their works, respectively [22-24].

Figure 3(a) and Figure 3(b) show the graph of direct and indirect optical band gaps. The variations of indirect and direct optical band gaps are shown in Table 1. Indirect and direct optical band gaps of the glass samples were found to be varied with the Sm_2O_3 content. These changes may be due to the variations in the amount of bridging oxygen (BOs) and non-bridging oxygen (NBOs) in the glass system. According to Fares et al., the decrement of NBOs caused a reduction in glass polarizability and increment of the optical band gap [25]. This was due to the fact that NBOs bound an excited electron less tightly as compared to BOs. Therefore, NBOs tends to be more polarisable than the BOs. Decrement of E_{opt} might be caused by weaker bond strength of Sm_2O_3 as compared to other chemical oxide in the glass. As a result, it was easier for the electrons to jump into the conduction band. The existence of trivalent electrons, Sm^{3+} ions caused the increment in the number of free electrons in the glass network. This will cause electrons to localise in deep energy levels and contributed to the declining of E_{opt} [26]. Table 1 also shows the results of Urbach energy (ΔE). Urbach energy gives information regarding to defects and disorderness of the glass network [27]. As tabulated in Table 1 as well as in the plotted graph of $\ln \alpha$ versus photon energy, $\hbar\omega$ is shown in Figure 4, the values of the Urbach energy were found to lay between 0.112 eV to 0.694 eV for the glass samples which were in agreement with the results found with other oxide glass, such as $\text{P}_2\text{O}_5\text{-TeO}_2$, $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5\text{-TeO}_2$ (0.17-0.67 eV) and $\text{TeO}_2\text{-MgO-Na}_2\text{O-Nd}_2\text{O}_3$ (0.12-0.21 eV), depending on glass composition [28, 29]. The Urbach energy, ΔE , was measured from the reciprocal of the linear region slope (in lower photon energy) of the curves.

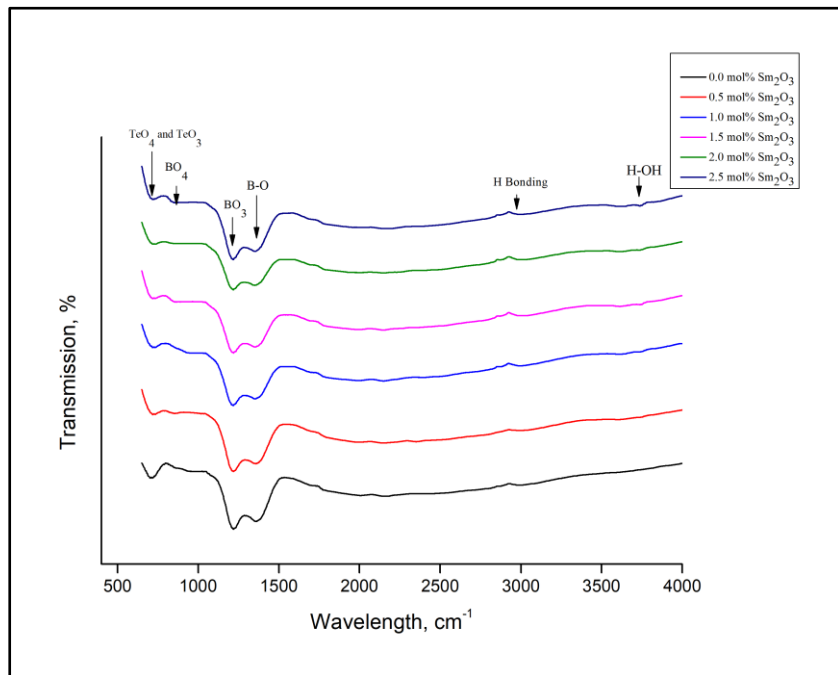


Figure 1. FTIR spectra of the Sm^{3+} doped zinc borotellurite glasses

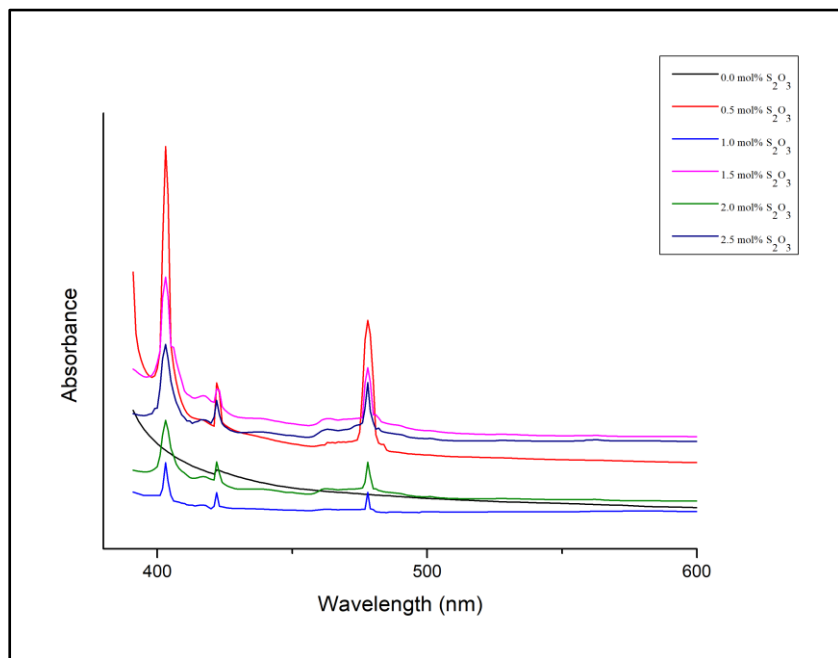


Figure 2. Normalised optical absorption spectra of glasses with different mol% Sm_2O_3

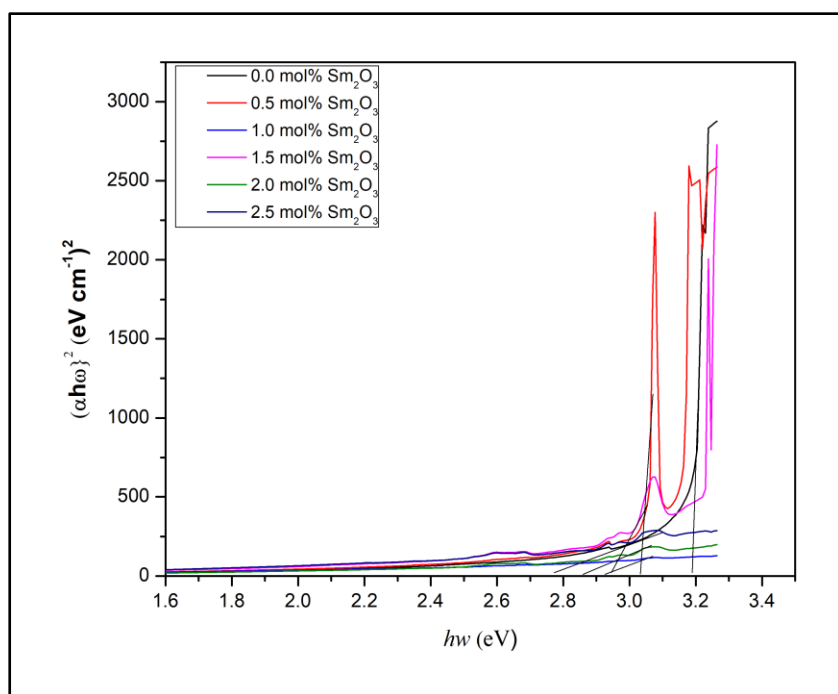


Figure 3(a). Plot of $(\alpha h\omega)^2$ versus $h\omega$ for direct band gap of $(70-x)\text{TeO}_2\text{-}20\text{B}_2\text{O}_3\text{-}10\text{ZnO-xSm}_2\text{O}_3$ glass system

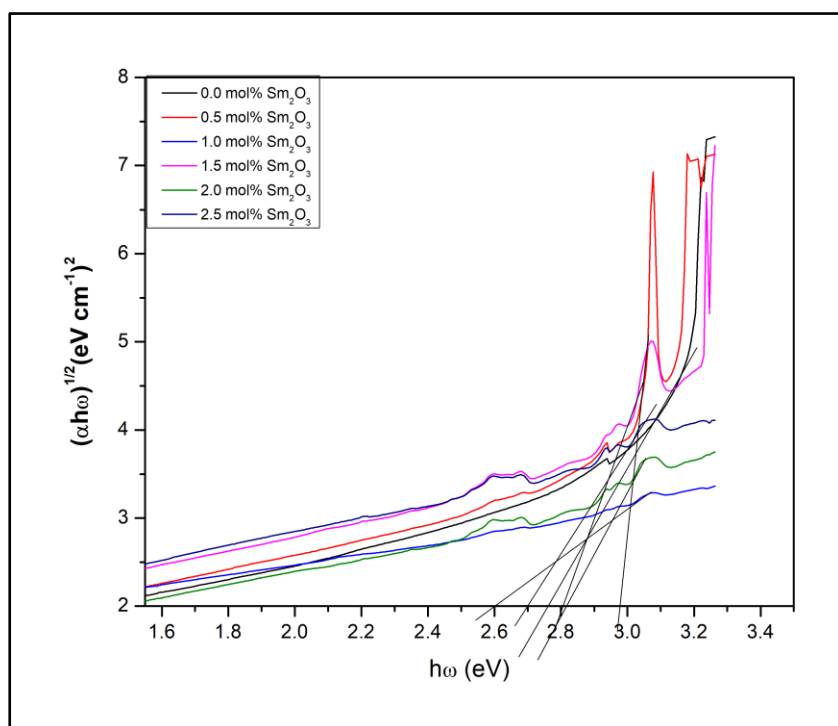


Figure 3(b). Plot of $(\alpha h\omega)^{1/2}$ versus $h\omega$ for indirect band gap of $(70-x)\text{TeO}_2\text{-}20\text{B}_2\text{O}_3\text{-}10\text{ZnO-xSm}_2\text{O}_3$ glass system

Table 1. Indirect E_{opt} , direct E_{opt} and Urbach energy (ΔE) of the glass samples

Samples No.	Indirect E_{opt} (eV)	Direct E_{opt} (eV)	Urbach Energy, ΔE (eV)
S1	3.198	2.815	0.644
S2	3.036	2.982	0.440
S3	2.768	2.605	0.112
S4	2.946	2.812	0.488
S5	2.868	2.755	0.694
S6	2.938	2.714	0.618

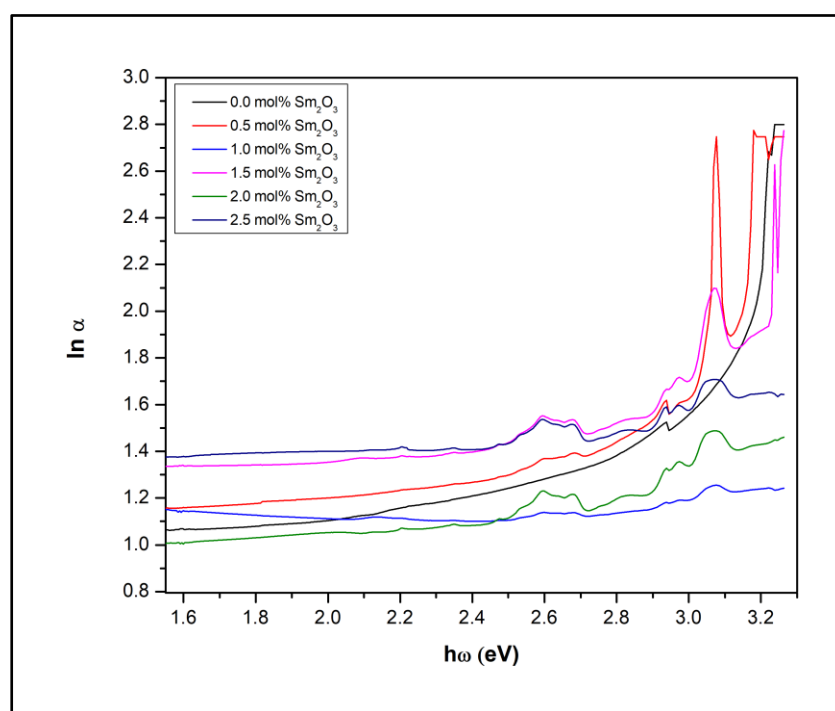


Figure 4. Plot of $\ln \alpha$ versus $h\omega$ for Urbach energy of $(70-x)\text{TeO}_2-20\text{B}_2\text{O}_3-10\text{ZnO}-x\text{Sm}_2\text{O}_3$ glass system

Conclusion

Sm^{3+} ions doped zinc borotellurite glasses were prepared and their structural and optical properties were studied and reported. The FTIR revealed the presence of asymmetric stretching vibrations of B-O bonds in BO_3 trigonal, BO_4 tetrahedral units and $\text{B}-\text{O}^-$ trigonal, Te-O bonds in trigonal pyramid (TeO_3) and trigonal bipyramid (TeO_4) units and the hydroxyl groups in the prepared glasses. The absorption spectra showed that the

strongest absorption occurred at 480 nm. The direct and indirect optical band gaps were found to vary independently with Sm_2O_3 contents.

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