STRUCTURAL PROPERTIES OF CERIUM OXIDE DOPED ZINC BOROTELLURITE GLASS

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Abstract

Zinc borotellurite glasses doped with CeO_2 ($\{[[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}]\}_{1-x}\{CeO_2\}_x$ where x = 0,1,2,3,4 and 5 mol%) were prepared using melt-quenching technique. The effect of cerium oxide was investigated by studying the structural properties of the glass system. Results showed that the density of glasses increased while the molar volume decreased with the addition of CeO_2 from 1 until 5 mol%. The increment in density could be attributed to the higher molecular weight of cerium oxide while the reduction in molar volume indicated the tightening effect that occurred in the glass network. Fourier Transform Infrared Spectroscopy (FTIR) analysis exhibited absorption bands for tellurite and borate network. After the deconvolution process, the band area for each structural unit in the glass network was calculated. The changes in the band area of TeO_4 and BO_4 were found to be independent to the composition of cerium oxide. The amorphous nature of the prepared glasses was confirmed using X-ray diffraction (XRD). The changes on all of the data were elucidated and related to the modifications in the structural network.

Keyword: Cerium; Density; FTIR; Molar volume; Tellurite glass; XRD

Introduction

Nowadays, glass has become a very important material in our daily life. Glass is different from the other types of solids as it possesses a disordered atomic structure which is also known as amorphous (literally meaning "without form") nature (Callister & Rethwisch, 2011). Due to its ability to transmit light, glass has been widely used for new applications such as in communications, photonics and electronics. For example, the use of glass for fibre optic has revolutionised the telecommunication industry by the replacement of copper wire with fibre optic. This then enables the transmission of flaw-free data throughout the world (Shelby, 2005). Tellurite glass (TeO_2) has attracted the attention of many researchers due to its advantages

compared to the other types of glass. The high rare earth solubility of this glass can solve the problem of silicate glass while its non-hygroscopic nature complements the weaknesses of borate and phosphate glasses (Mohamed et al., 2021; Upender et al., 2012; Yoshida et al., 2004). Besides, it also has a low melting temperature, high IR transmission, high refractive index and low phonon energy (Akshatha et al., 2014; Halimah et al., 2005; Raju et al., 2011). However, TeO_2 glass is known to have a difficulty in forming glass on its own. Hence, it needs to be added with another chemical to improve the glass-forming ability which in the present study are B_2O_3 and ZnO.

Recently, there has been a growing number of researches done on zinc borotellurite glass (Azlan et al., 2013; Eevon et al., 2016; Faznny et al., 2016; Hajer et al., 2014; Hazlin et al., 2017). However, different types of rare earth oxides were used in the previous studies and not much research has been done on cerium doped zinc borotellurite glass. In this research, the investigation focused on the effect of cerium on the structural properties of zinc borotellurite glass. The structural studies of this glass are believed to be important as it can give an insight on how cerium oxide participates in the glass network which then leads to the changes of the other properties of the glass system.

Materials and Methods

Glass samples with the composition of $\{[[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}]\}_{1-x}\{CeO_2\}_x$ were produced by using the melt-quenching technique with x varied from 0.00 until 0.05 mol. The chemical oxides that were used in this study were obtained from Alfa Aesar, with purity of 99.9%, 99.99%, 97.5% and 99.99% for CeO_2, ZnO, B_2O_3 and TeO_2 respectively. Firstly, all of the chemical oxides were weighed using the Dragon 204 Mettler Toledo Electronic Balance. Then, the chemicals were mixed in an alumina crucible, stirred, and ground simultaneously for 30 minutes to get a homogeneous mixture. After that, the crucible was put into the first furnace to undergo pre-heating process at 400ºC. This process was done to vaporise any moisture that might be present in the mixture. After one hour, the crucible was put in the second furnace for a melting process at 900ºC for one hour. Next, the molten was poured into a stainless steel mould which had been pre-heated at 400ºC. The mould was then annealed in the first furnace at 400ºC. After two hours, the furnace was turned off and the sample was left overnight to let it cool down to room temperature. On the next day, the sample was taken out from the furnace. Some of the samples were ground into powder form for FTIR and XRD analyses.

Result and Discussion

X-Ray Diffraction

The XRD pattern of $\{[[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}]\}_{1-x}\{CeO_2\}_x$ glass is as shown in **Error! Reference source not found.**. A broad hump is present in the pattern while no sharp peak can be observed. A similar result can also be detected for $[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{0.7}[ZnO]_{0.3}$ without any dopant (Azlan et al., 2014). This indicates that all the glasses have an amorphous nature (Azuraida et al., 2015; Dias et al., 2016; Yusoff & Sahar, 2015). Besides, the hump position at around 20º actually marked the position of where crystalline peak is most likely to appear if the glass is devitrified (Thomas, 2013).

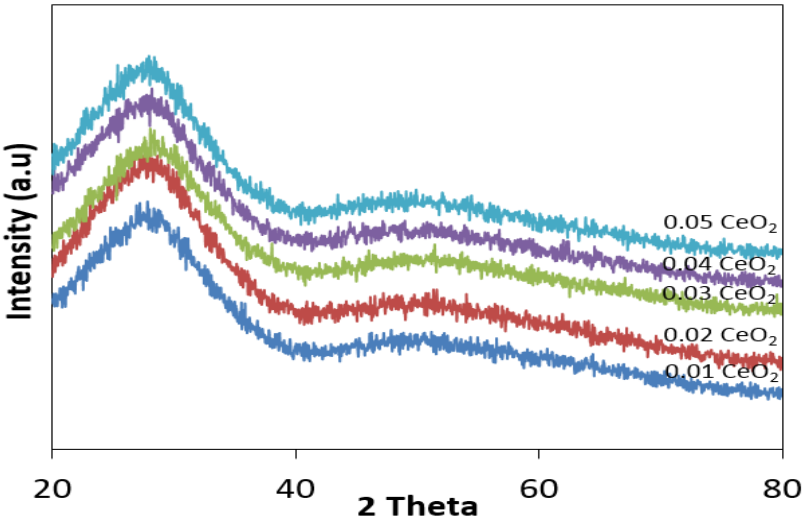

Figure 1 XRD pattern of CeO_2-doped ZnO-B_2O_3-TeO_2 glass system

FTIR analysis

The FTIR spectra of the $\{[[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}]\}_{1-x}\{CeO_2\}_x$ (**Figure 2**) showed five bands situated at 600-640 cm^{-1}, 850-1100 cm^{-1} and 1200-1400 cm^{-1} that corresponded to TeO_4, BO_4 and BO_3 structural units. Similar bands could also be detected for glass with 0 mol% of CeO_2. In addition, absorption bands at 281 cm^{-1} and 414-421 cm^{-1} could also be observed. These bands corresponded to ZnO_4 structural units (Azlan et al., 2014; Boda et al., 2015). The disappearance of these bands as CeO_2 was added might be due to the breaking of Zn-O bonds. Hence, ZnO acted as network modifier and became interstitial atoms. This was also believed to be the reason behind the absence of Ce-O bonds. Next, the spectra were deconvoluted to distinguish and calculate the area of each peak. This was done to get the exact concentration for each structural unit and to observe their variation clearly as Ce was added. After the deconvolution process, it was noted that the spectra consisted of six absorption bands. Details of the information regarding this matter are as recorded in **Table 1** while

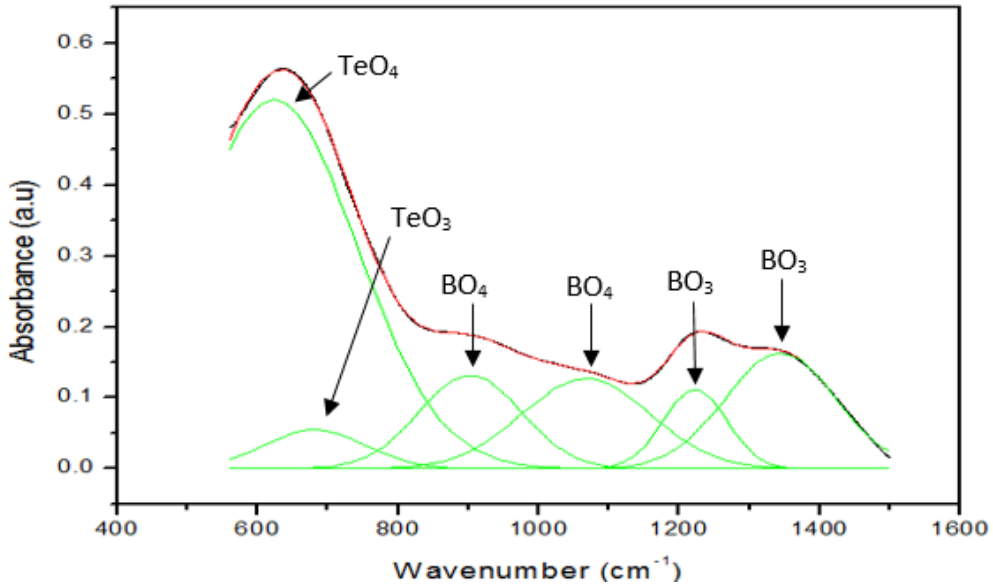

Figure 3 shows the deconvolution spectrum of x=0.01 mol. It was found that the effect of cerium oxide in the glass network was independent to its composition. The variation of these structural units then led to the changes of other properties of the glass system.

Table 1 Band center (B), band area (A) and assignments for CeO_2-doped ZnO-B_2O_3-TeO_2 glass system

CeO_2 mol content		**Band center, B (cm^{-1}) and band area, A (%)**					
0.00	B	617.79	679.18	908.12	1014.80	1221.60	1348.70
	A	15.30	54.70	0.45	0.09	7.80	21.66
0.01	B	623.37	680.66	902.46	1067.40	1222.40	1344.00
	A	65.77	4.23	7.37	8.91	3.88	9.84
0.02	B	631.80	657.62	899.29	1055.30	1220.90	1347.60
	A	65.67	4.33	5.70	9.82	4.69	9.78
0.03	B	604.06	672.07	891.04	1055.10	1218.70	1338.50
	A	54.36	15.64	5.86	10.93	3.10	10.11
0.04	B	611.49	669.29	918.23	1073.60	1214.90	1346.90
	A	65.79	4.21	7.29	6.72	6.06	9.93
0.05	B	600.84	674.10	918.99	1071.40	1214.00	1346.20
	A	64.43	5.57	5.40	7.67	5.94	10.99
Assignment		TeO_4 trigonal bipyramids	TeO_3 trigonal pyramid	Stretching modes of $[BO_4]^-$ tetrahedral borons (Elkhoshkhany et al., 2020)		Stretching modes of $[BO_3]^0$ triangular borons (Elkhoshkhany et al., 2020)	

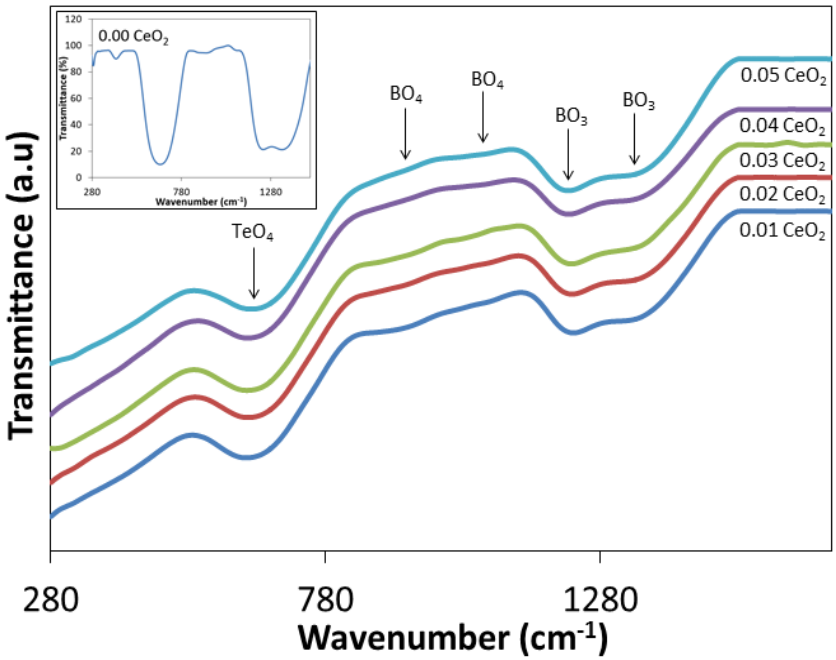

Figure 2 FTIR spectra of CeO_2-doped ZnO-B_2O_3-TeO_2 glass system

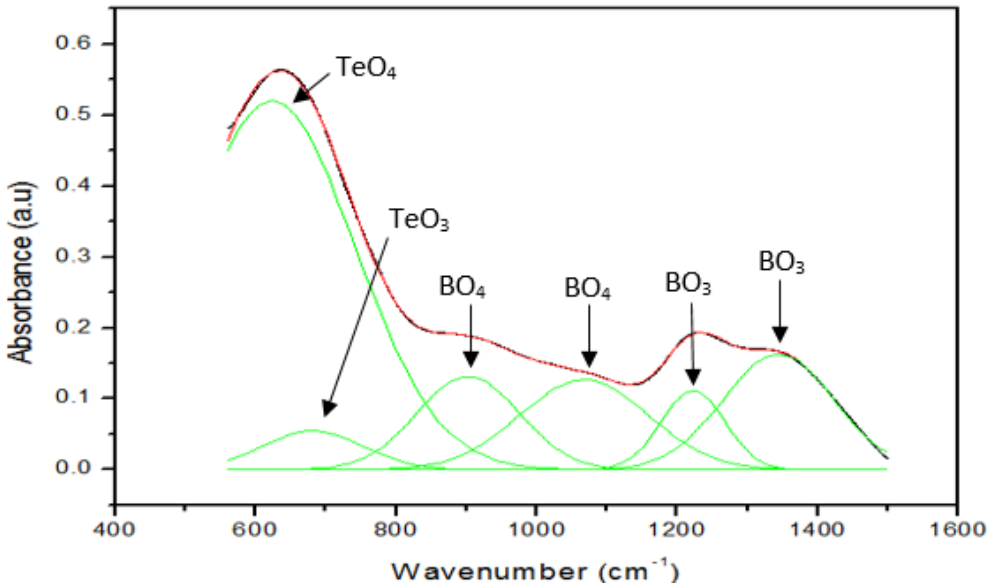

Figure 3 Deconvoluted FTIR spectra of $\{[[(TeO_2)_{0.7}\ (B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}]\}_{0.99}\{CeO_2\}_{0.01}$ glass system

Density and molar volume

The measured results of density and molar volume are as written in **Table 2**. It shows that the value of density increases with the increment of CeO_2 concentration. This indicates that the network structure became more compact as cerium was added. The elevation was probably due to the higher molecular weight of cerium oxide (172.118 g/mol) compared to the other chemical compounds that were used in this study. As the heavier compound replaced the lighter compound, the total molecular weight of the glass samples increased, hence the density increased as well. Besides that, the densification of the glass might also be attributed to the lower ionic radii of Ce ions compared to oxygen ions. This feature enables them to be inserted into the interstitial spaces between the atoms and cause the glass to become denser.

Table 2 Density and molar volume of cerium doped zinc borotellurite glass system

CeO_2 composition (mol)	ρ (g/cm^3)	m_v (cm^3/mol)	Reference
0.00	3.69	31.75	(Azlan et al,2013)
0.01	4.60	25.62	
0.02	4.62	25.63	
0.03	4.64	25.61	
0.04	4.67	25.58	
0.05	4.69	25.57	

Molar volume (m_v) is another parameter used to determine the compactness of material. In this study, m_v was observed to have a decreasing trend as CeO_2 was incorporated into the glass system with a slight increment at 0.02 mol of cerium. The augmentation of molar volume might be due to the formation of free volume inside the glass network. The free volume was created by the greater length of Ce-O bond (0.248 nm) and its high coordination number (8). Besides that, the production of non-bridging oxygen also contributed to the rises of m_V. Non-bridging oxygen (NBO) was produced when BO_4 and TeO_4 structural units were converted into BO_3 and

TeO_3 respectively, which in turn caused the network structure to loosen up and become less compact. The decrement of molar volume at 1 mol% of cerium concentration and when it exceeded 2 mol% specified that there was a tightening process occurring inside the glass system. According to(Kaur et al., 2012) and(Singh et al., 2012), CeO_2 has a contracting effect in a glass. The incorporation of cerium caused the interatomic spacing in the network structure to reduce and this can be attributed to the production of Ce^{4+} ions which has higher cation field strength (0.80) than Ce^{3+} ions (0.54) (Herrmann et al., 2015). In addition, the formation of bridging-oxygen at this point can also cause the drop of m_v. The area of TeO_4 and BO_4 was found to increase at 1 and 4 mol% and at 1 and 3 mol% of CeO_2 respectively, thus supporting this reasoning.

Conclusion

The $\{[[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.7}(ZnO)_{0.3}]\}_{1-x}\{CeO_2\}_x$ glass system was successfully prepared using melt-quenching technique with x was varied from 0.00 until 0.05 mol. The densities of the glasses exhibited an increasing trend with the addition of cerium oxide while molar volume showed an opposite trend. The absorption bands of TeO_4, TeO_3, BO_4 and BO_3 structural units were revealed in FTIR analysis while the XRD pattern confirmed the amorphous nature of all the glass samples. In summary, it can be concluded that the incorporation of cerium oxide results in the changes of the network structure which in return produce glass with higher density and more compact.

Acknowledgement

The author gratefully acknowledged the financial support and laboratory equipment provided by Universiti Putra Malaysia, Universiti Pertahanan Nasional with Short Term Grant UPNM/2019/GPJP/2/SG/6 and Ministry of Higher Education (MOHE) Malaysia.

Conflict of interests

Authors hereby declare that there is no conflict of interests with any organisation or financial body in supporting this research.

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