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Spectroscopic studies of TeO_2–ZnO–Er_2O_3 glass system

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Abstract Series of glass based on the (80 – *x*)TeO_2–20ZnO–(*x*)Er_2O_3 system (0.5 mol% ≤ *x* ≤ 2.5 mol%) has successfully been made by melt quenching technique. The optical properties of glass have been investigated by means of IR and Raman spectroscopy. It is observed that as the Er_2O_3 content is being increased, the sharp IR absorption peaks are consistently shifted from 650 to 672 cm^{-1} while the Raman shift intensity around 640–670 cm^{-1} is decreases but increases around 720–740 cm^{-1}. It is found out that both phenomenons are related to the structural changes between the stretching vibration mode of TeO_4 tbp and TeO_3 tp, and bending vibration mode of Te–O bonds in the glass linkages.

Introduction

Tellurite glasses are known to be an important amorphous system that has many potential commercial applications. They exhibit a range of unique properties not only due to their low transition temperature but also to their excellent infrared transmission [1] particularly in the range of 0.4–6.0 μm [2]. It has also been reported that these glasses are excellent candidates for hosting rare-earth ions since they provide a low-phonon-energy environment to minimize the non-radiative losses as well as possessing good chemical durability and optical properties [3]. These would give them a potential application in pressure sensors or a new laser host. The erbium-doped tellurite glasses also have shown optical and chemical properties suitable for optical applications [4, 5], and can be use as laser light modulators [6] and thermally stable for fiber drawing [7].

Studies on the TeO_2–ZnO glass system have been focused on the glass formation and structural properties [2, 8, 9]. A similar study has also been done in TeO_2–ZnO–$ZnCl_2$ glass system [10, 11]. It has been shown that these glasses possess two types of basic structure unit, namely TeO_4 trigonal bipyramids (tbp) and TeO_3 trigonal pyramid (tp) depending on the content and type of the modifier being used [12]. However, not much research on the characteristic of the tellurite—Er_2O_3 glass has been reported in the literature.

It is therefore the aim of this paper to present the latest development of (80–*x*)TeO_2–20ZnO–(*x*)Er_2O_3 system. All the results will be discussed with respect to their composition.

Experimental

Tellurite glasses based on the (80–*x*)TeO_2–20ZnO–(*x*)Er_2O_3 system (0.5 mol% ≤ *x* ≤ 2.5 mol%) was prepared by melt quenching technique. Detail description on the glass preparation has been reported elsewhere [13].

The IR transmission spectra have been observed by using the Perkin–Elmer GX FT–IR spectroscopy. Typically about 2 mg of a finely ground glass sample

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is mixed with 200 mg of KBr before being pressed at 40 kN to obtain a pallet discs of about 15 mm in diameter. A scan in the spectral range of 400–4,000 cm^{-1} at the resolution of 2 cm^{-1} has been carried out.

The Perkin–Elmer GX FT Raman spectroscopy has been used to observe the Raman spectra. A relatively fine glass powder is used for measurement of Raman spectroscopy at laser wavelength of 810 nm and typical power of 350 nW. Raman spectra were recorded in the range of 100–2,000 cm^{-1}.

Results

The IR transmission spectra of glasses are given in Fig. 1 and their corresponding absorption bands are summarized in Table 1. From Fig. 1, it can clearly be seen that a sharp absorption peaks around 650 cm^{-1} has steadily been shifted to 672 cm^{-1} as the Er_2O_3 content is gradually increased. It is also observed that the samples exhibit a small absorption peaks around 770 and 1,115 cm^{-1}.

The Raman spectra of the glasses are shown in Fig. 2 and the corresponding peaks shifts are summarized in the Table 1. From Fig. 2 it can clearly be seen that the peaks around 410–440 cm^{-1} occur in all glasses. However, when the Er_2O_3 content is increased to more than 0.5 mol%, the Raman intensity around 640–670 cm^{-1} decreases while the intensity around 720–740 cm^{-1} increases.

Discussion

As can be observed from Table 1, the absorption peaks consistently shift from 462 to 470 cm^{-1} with the increase of the Er_2O_3 content and this can be assigned to the Zn–O tetrahedral bond [14]. It should however be noted that there are many small peaks occur within these ranges as the Er_2O_3 content is being increased. The occurrence of these small peaks is presumably due to the deformation of the Te–O bond vibration [15].

The broad peaks that were observed around 650 and 770 cm^{-1} can be ascribed to the mixing structures of TeO_3 groups, symmetric TeO_4 groups and deformed TeO_4 groups [16]. However, as the Er_2O_3 content increases (in S2–S5), the sharp absorption peaks shift from 650 to 672 cm^{-1}. For Er_2O_3 content,

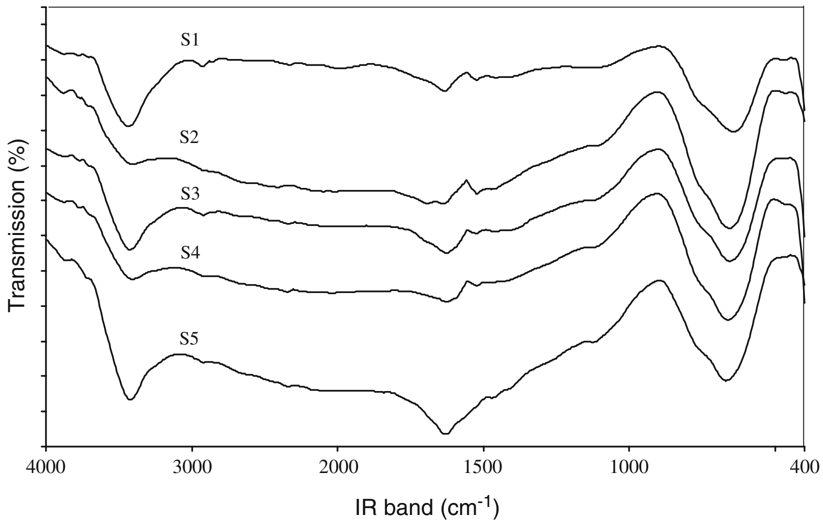

Fig. 1 The infrared transmission spectra of TeO_2–ZnO–Er_2O_3 glasses at various compositions

Table 1 The IR bands position and Raman peaks shift of the TeO_2–ZnO–Er_2O_3 glass system

Sample no	Composition (mol%)			IR bands (cm^{-1})	Raman shift (cm^{-1})
	TeO_2	ZnO	Er_2O_3		
S1	80.0	20.0	0.0	462; 650; 768; 1111; 1635; 3431	433; 642; 720
S2	79.5	20.0	0.5	462; 658; 768; 1115; 1635; 3416	433; 651; 725
S3	79.0	20.0	1.0	470; 661; 772; 1118; 1627; 3416	293; 424; 651; 725
S4	78.0	20.0	2.0	470; 665; 772; 1118; 1627; 3416	280; 412; 671; 733
S5	77.5	20.0	2.5	470; 672; 776; 1118; 1627; 3424	260; 412; 671; 733

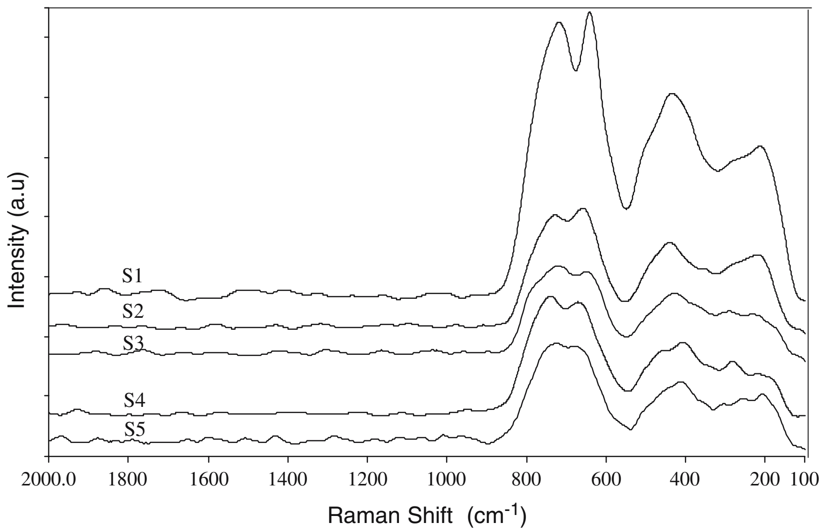

Fig. 2 Raman spectra of TeO_2–ZnO–Er_2O_3 glasses at various compositions

0.5 mol% ≤ x ≤ 1.0 mol%, the absorption peak is slightly blue shift [16]. At the same time, the shoulder at 776 and 768 cm^{-1} started to emerge. This can be assigned to the TeO_3 tp of $ZnTeO_3$ [10].

Meanwhile, the absorption peaks around 1,115 cm^{-1}, which corresponds to the Te–O–Zn linkages [14], seem do not affected by the variation in composition.

Another well-known IR absorption peaks occur around 1,600 and 3,400 cm^{-1}. These are assigned to a stretching vibration of the hydroxyl group participating in the strong metal bonding as well as in the hydrogen bonding, respectively [15]. The existence of these groups is very common to the oxide glass system.

As can be seen in Fig. 2, the Raman peak intensity around 640–670 cm^{-1} decreases rapidly with the decreasing of TeO_2 content. Meanwhile, it can also be observed that the peaks intensity around 720–740 cm^{-1} increase with the increasing in Er_2O_3 content. These might be due to the perturbation of the tellurite of TeO_4 tbp unit into TeO_3 tp unit by the intermediate coordination of TeO_{3+1} [8, 17–19]. These features would clearly indicate that the number of the TeO_3 tp structural unit increases with the increasing of Er_2O_3 contents. This is true since the peaks intensity around 720–740 cm^{-1}, which is due to the stretching vibration of the TeO_3 tp units [18] increases with the Er_2O_3 content. Therefore, it can be said that the increasing in Er^{3+} in the glass would creates more TeO_3 tp units. This is consistent with the previous IR result at the absorption peaks around 650 and 770 cm^{-1}, which have been ascribed to the stretching vibration of equatorial and axial Te–O bonds in the TeO_4 tbp unit and TeO_3 tp [10].

The Raman peaks intensity around 640–670 cm^{-1}, which is assigned to the stretching vibration of TeO_4 tbp units is decreases as the Er_2O_3 contents increases. These trends is consistent with the destruction of the TeO_4 group in the network.

Meanwhile, the peak intensity of Raman shifts around 410–440 cm^{-1} decreases as the Er_2O_3 content increases. A decrease in the peak intensity would suggest the destruction of the Te–O–Te (or O–Te–O) linkages thus reduces the Te–O–Te linkages out of a continuous network of TeO_n (n = 4, 3 + 1, and/or 3) entities thus consistent with the previous observations [17].

Conclusions

From the above discussions, some conclusions may be drawn.

(i) A wide and stable glass formation range can be obtained in the $(80 - x)TeO_2$–20ZnO–$(x)Er_2O_3$ system (0.5 mol% ≤ x ≤ 2.5 mol%).

(ii) The broad IR absorption band around 650–672 cm^{-1} and 768–776 cm^{-1} can be ascribed to the stretching vibration of equatorial and axial Te–O bonds in the TeO_4 tbp unit and TeO_3 tp, respectively.

(iii) As the Er_2O_3 content increases, the Raman peaks intensity around 642–671 cm^{-1} decreases while the peaks intensity around 720–733 cm^{-1} increases. These are presumably due to the conversion of the TeO_4 tbp units into TeO_3 tp units.

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