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Effect of the introduction of vanadium pentaoxide in phospho-tellurite glasses containing gadolinium ions

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Abstract A range of phospho-tellurite glasses containing gadolinium was prepared and infrared absorption spectra were measured. Structural changes, as recognized by analyzing band shapes of IR spectra, revealed that Gd_2O_3 causes a higher extent of network polymerization as far as $x \leq 15$ mol% because the conversion of $[TeO_4]$ to $[TeO_3]$ structural units is supported by the increase of metaphosphate structural groups. While for x between 20 and 30 mol% Gd_2O_3 show some drastic structural modifications which lead to the increase in the glass fragility. Thus the addition of V_2O_5 resulted in gradual depolymerization of the phosphate chains and formation of short phosphate units, which are linked to vanadium through P–O–V bonds. The formation of P–O–V bonds increases the cross-link between the phosphate chains and the bending mode of Te–O–Te or O–Te–O linkages.

Introduction

Phosphorus pentaoxide glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficients, low melting and softening temperatures, and ultra-violet transmission [1–5]. However, the poor chemical durability, high hygroscopic, and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in a wide range of technological applications. In recent years, many researches on improving the physical properties and the chemical durability of phosphate glasses, by introducing a number of heavy metal oxides into P_2O_5 glass network [6–9], were carried out.

Tellurium oxide is a heavy metal oxide and when it is introduced in the glass matrix, it may influence the physical properties such as refractive index, thermal expansion coefficient, chemical resistance, infrared transmittance of the glasses, and further makes the glasses suitable for use as devices for communication and advanced computer applications.

When doped with a different kind of rare earth ions, these glasses find wide use in high power laser technology, sensor, optical switching, and amplifiers for fibre communications [10–13].

The present investigation is aimed at understanding the structural role of Gd_2O_3 and V_2O_5 in TeO_2–P_2O_5 glass network by studying FTIR spectra.

Experimental

The $x\mathrm{Gd_2O_3} \cdot (100 - x)[0.7\mathrm{TeO_2} \cdot 0.3\mathrm{P_2O_5}]$ glasses were prepared by mixing together specific weights of TeO_2, P_2O_5, and Gd_2O_3 in a ceramic crucibles. The crucible was transferred to a furnace for 30 min at 1,100 °C. The sample with the higher content of gadolinium oxide was subject to the treatment with 5 mol% vanadium pentaoxide contain and the prepared at 1,000 °C for 10 min into a furnace.

The samples were analyzed by means of X-ray diffraction using a XRD-6000 Shimadzu Diffractometer, with a monochromator of graphite for Cu-Kα radiation ($\lambda = 1.54$ Å) at room temperature.

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The IR absorption spectra of the studied glasses were measured for each glass sample over the range 400–1,400 cm^{-1}, of wavenumber. A JASCO FTIR 6200 spectrometer was used in conjunction with the potassium bromide, KBr, disc technique. Samples of glass weighing 0.002 g were mixed and ground with 0.300 g KBr. After which the mixture was pressed at 10 tons for 3 min under vacuum, to yield transparent discs suitable for mounting in the spectrometer. The precision of the absorption band maxima is ±2 cm^{-1}.

Results and discussion

The X-ray diffraction patterns obtained did not reveal any crystalline phase in the samples (Fig. 1).

The FTIR spectra of $x\mathrm{Gd_2O_3} \cdot (100 - x)[0.7\mathrm{TeO_2} \cdot 0.3\mathrm{P_2O_5}]$ recorded at room temperature is shown in Fig. 2; the spectra exhibited three groups of absorption bands due to different structural units of TeO_2, P_2O_5, and Gd_2O_3.

The bands located around 460 cm^{-1} in the range of 610–680 and 720–780 cm^{-1} are assigned the bending mode of Te–O–Te or O–Te–O linkages, the stretching mode [TeO_4] trigonal pyramidal with bridging oxygen, and the stretching mode of [TeO_3] trigonal pyramidal with non-bridging oxygen, respectively [14–16].

Spectra show a clearly resolved band at about 625 cm^{-1}, which is identified to be due to the vibrations of [TeO_4] units. By increasing the concentration of gadolinium ions up to 15 mol%, the intensity of this band is observed to decrease systematically, indicating a gradual conversion of four coordinated Te^{+4} ions into three coordinated tellurium ions forming [TeO_3] units (760 cm^{-1}) [14–16]. The intensity of this band is observed to increase with the shifting of the centre towards slightly smaller wavenumbers (750 cm^{-1}). After that the intensity of this band is found to decrease at a gadolinium concentration >20 mol%.

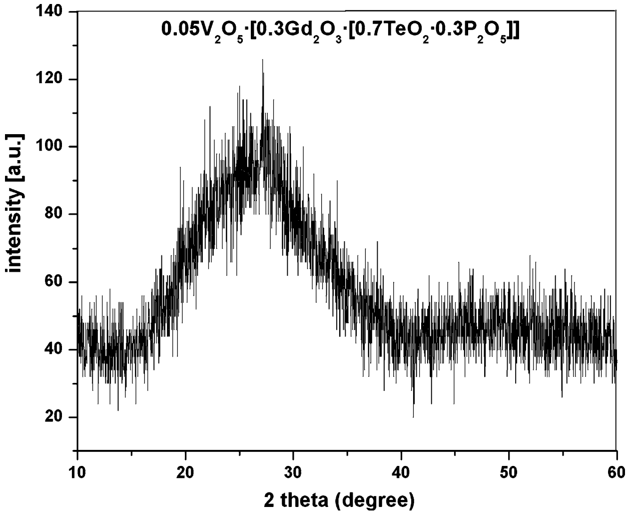

Fig. 1 X-ray diffraction pattern for $0.05\mathrm{V_2O_5} \cdot [0.3\mathrm{Gd_2O_3} \cdot 0.7[0.7\mathrm{TeO_2} \cdot 0.3\mathrm{P_2O_5}]]$ glasses

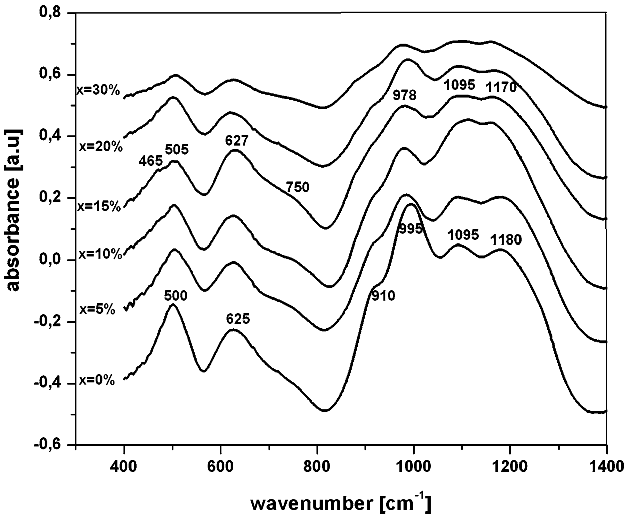

Fig. 2 FT-IR spectra of the $x\mathrm{Gd_2O_3} \cdot (100 - x)[0.7\mathrm{TeO_2} \cdot 0.3\mathrm{P_2O_5}]$ (for x = 0–30 mol%)

The FTIR spectrum of each glass has also exhibited the following four groups of bands due to phosphate structural units:

(i) A prominent band centered in the region 1,200 cm^{-1} is due to P=O stretching. This region may also consist of bands due to antisymmetric vibrations of PO_2 groups. The position of this band is found to be shifted towards lower wavenumber (~1,170 cm^{-1}) with the increase of the Gd_2O_3 concentration.

(ii) A band at 1,100 cm^{-1} identified due to vibrations of PO_2 of metaphosphate groups [17]. The intensity of this band increases up to x = 10 mol% Gd_2O_3 after which it decreases slowly.

(iii) Third group of band located at about 970 cm^{-1} was assigned to [PO_4] of orthophosphate groups vibrations. Its intensity decreases with increasing gadolinium ions concentration.

(iv) Another band centered at about 530 cm^{-1} is attributed to deformation modes of P–O from [PO_4] groups. The absorption band near 900 cm^{-1} is assigned to the asymmetric stretching mode [18].

Accordingly, the well defined band in the region ~625 cm^{-1} is an overlap of two vibrational modes, [TeO_3] trigonal pyramids and [TeO_4] trigonal bypiramids [19, 20]. This band preserved its shape, shifted to a higher wavenumber upon increasing the gadolinium oxide content up to 15 mol% in the glass and a shoulder is appeared at ~750 cm^{-1} on curves corresponding to the glasses containing 5, 10, 15 mol% Gd_2O_3. This indicates the separation of [TeO_3] units and the transformation of [TeO_4] to [TeO_3] structural units. This conversion is supported by the increase of metaphosphate structural units with the gradual addition of gadolinium oxide up to 15 mol%.

Hence, the increase in concentration of gadolinium ions ($5 \leq x \leq 15$ mol%) leads to an increase in the polymerization visibly of the phosphate network because the intensity of the groups of bands due to ortophosphate structural units are more reduced and the decrease in the number of the non-bridging oxygen atoms would increase the connectivity of the glass network. Such a behavior, namely the increase of the polymerization degree of the structural units with increasing the rare earth ion content was previously reported based on IR and XPS spectroscopy data for the Nd_2O_3–$3Bi_2O_3$–PbO [21, 22], Gd_2O_3–$4Bi_2O_3$–B_2O_3 [23, 24], Eu_2O_3–$4Bi_2O_3$–B_2O_3 [25], and Eu_2O_3–$3B_2O_3$–PbO glasses [26].

In brief, structural changes as recognized by analyzing band shapes of IR spectra, revealed that Gd_2O_3 causes a higher extent of network polymerization as far as $x \leq 15$ mol%, while for x between 20 and 30 mol% showed some drastic structural modifications which lead to the increase in the glass fragility and probably decrease in the glass transition temperature. These modifications are: (i) the decrease of the relative intensity of the absorption band corresponding to the P=O stretching and the shifting of the band position towards lower wavenumbers and (ii) the increase of ortophosphate structural units.

Accordingly, we assume that the glass structure is made up in especially from trigonal bipyramidal [TeO_4] groups with lone pair of electrons, the tetrahedral phosphate anion [PO_4] (in specially orthophosphate and metaphosphate groups), and [TeO_3] trigonal pyramidal units.

The FTIR spectrum of the $0.05V_2O_5 \cdot [0.3Gd_2O_3 \cdot 0.7[0.7TeO_2 \cdot 0.3P_2O_5]]$ glass is shown in Fig. 3. The strong and broad band at 900–1,200 cm^{-1} seems to be a combined effect of both V_2O_5 and P_2O_5.

It is known that the characteristic vibrations of the isolated vanadium–oxygen bonds in the IR spectrum are in 900–1,020 cm^{-1} range [27–29]. The band in the range of 970–980 cm^{-1} is assigned to the vibrations of the VO_2 groups of the [VO_4] polyhedra. The band located at about 1,020 cm^{-1} is related to the vibrations of the non-bridging V=O of the [VO_5] groups [29].

It has been observed that the addition of vanadium pentaoxide in the glass composition has resulted in the increment of the intensity of the following bands:

(i) The bending vibration of P–O bands from PO_4^{-3} groups are characterized by a broad band at 524 cm^{-1} [30];

(ii) The broad band located at ~769 cm^{-1} may be attributed to the symmetric stretching vibration of P–O–P rings. The prominent band centered at about ~740 cm^{-1} is assigned to the P–O–P linkage in pyrophosphate group ($P_2O_7^{-4}$) [31];

(iii) The band located at about 883 cm^{-1} is attributed to the asymmetric stretching of P–O–P groups, which confirms the chain structure of metaphosphate glasses. The intense band at ~1,155 cm^{-1} has been assigned to the symmetric stretching modes PO_2 of metaphosphate chains [32];

(iv) The strong band at ~1,094 cm^{-1} is attributed to asymmetric stretching of PO_3^{-1} groups in PO_4^{-3} units;

(v) The depolymerization of glass leads to the formation of short chain phosphates, characterized by band at ~1,220 cm^{-1} [32]. This band is assigned to vibrations of PO_2 in short chain phosphates, since that vibration mode is assigned at 1,000–1,240 cm^{-1} in tetrapolyphosphates ($P_4O_{13}^{-6}$) [33] and 1,215 cm^{-1} in tripolyphosphates ($P_3O_{10}^{-5}$) [34].

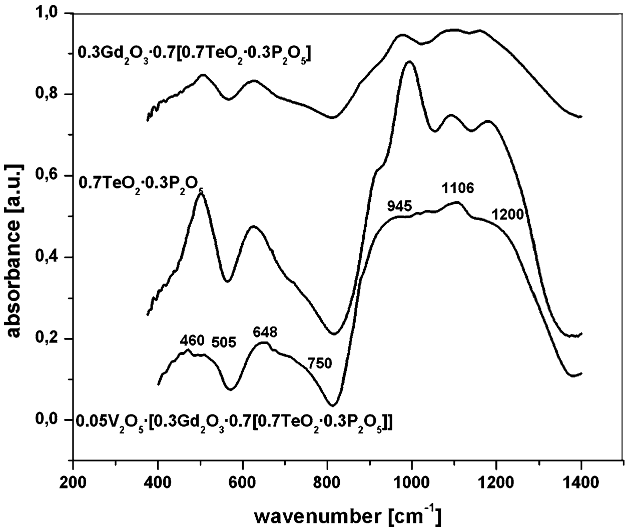

Fig. 3 FT-IR spectra of the $xGd_2O_3 \cdot (100-x)[0.7TeO_2 \cdot 0.3P_2O_5]$ (for $x = 0$ and 30 mol%) and $0.05V_2O_5 \cdot [0.3Gd_2O_3 \cdot 0.7[0.7TeO_2 \cdot 0.3P_2O_5]]$

These features indicate a decrease in the degree of polymerization of the network caused by weakening of the P–O–P bonds. The metaphosphate chains are broken into smaller groups of short chain phosphates such as $P_4O_{13}^{-6}$, $P_3O_{10}^{-5}$, and $P_2O_7^{-4}$, which are linked to vanadium through P–O–V bonds. The formation of P–O–V bonds increases the cross-link between the phosphate chains and the increase of the bending mode of Te–O–Te or O–Te–O linkages.

The gradual increase of gadolinium oxide in the glass up to 30 mol% results in the transformation of some trigonal bypyramids [TeO_4] to trigonal pyramids [TeO_3] units, and disappearance of the P=O stretching bond in [PO_4] tetrahedron. This in turn has led to a gradual increase in the openness and a decrease in the connectivity (layered structure instead of three-dimensional network) as evidenced by the observed decrease in relative intensity of IR absorption bands, the rapid homogeneity of the vanadium pentaoxide into glass network and increased fragility of studied glasses.

Conclusions

FTIR spectroscopy has been utilized in order to study structural changes produced by the variation of the Gd_2O_3 content in ternary $x\mathrm{Gd_2O_3}(100-x)[0.7\mathrm{TeO_2}\cdot 0.3\mathrm{V_2O_5}]$ glasses.

Structural changes produced by varying the Gd_2O_3 content of the samples consist in an increase of the extent of network polymerization up to 15 mol% and a drastic structural modification for $20 \le x \le 30\%$ lead to the increase in the glass fragility and the decrease in the glass transition temperature. This compositional evolution of the structure could be explained by considering that the excess of oxygen may be accommodated by the conversion of some $[TeO_4]$ to $[TeO_3]$ structural units and of orthophosphate into metaphosphate structural units. While for x between 20 and 30 mol% some drastic structural modifications lead to the increase in the glass fragility and the decrease in the glass transition temperature (because the vanadium containing glass was melted only for 10 min at 1,000 °C).

Thus the addition of V_2O_5 resulted in gradual depolymerization of the phosphate chains and formation of short phosphate units, which are linked to vanadium through P–O–V bonds. The formation of P–O–V bonds increases the cross-link between the phosphate chains and the increase of the bending mode of Te–O–Te or O–Te–O linkages.

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