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VIBRATIONAL STUDIES OF STRONTIUM ANTIMONY PHOSPHATE GLASS

Rosli Hussin, Nur Aimi Syaqilah Aziz, Aliff Rohaizat, Karim Deraman, W. Nurulhuda
W. Shamsuri, D.N. Fazliana Abdul Halim, M.S. Husin. N.E Ahmad,
I.H Hashim and Bakar Ismail

Phosphor Materials Research Group, Department of Physics,
Universiti Teknologi Malaysia, 81310 Skudai, Johor

ABSTRACT

Glass samples in a series of $60P_2O_5$-$x$$Sb_2O_3$-(40-$x$)SrO (95-$x$)$P_2O_5-5Sb_2O_3$-$x$SrO and (95-$x$)$P_2O_5$-$x$$Sb_2O_3$-5SrO with $5 \leq x \leq 35$ mol% were prepared using melt-quenching technique. The effect of SrO and Sb_2O_3 content on the structure of ternary Sb_2O_3-SrO-P_2O_5 ultraphosphate glass has been measured by means of X-ray Diffraction (XRD), Infrared and Raman Spectroscopy. The results from XRD patterns indicate that the compositions containing up to 35% of Sb_2O_3 and/or SrO formed as a glass easily and there were no crystalline phases detected. Spectra from IR and Raman Spectroscopy indicate shows the phosphate network of these glasses was composed of branching (Q^3), middle phosphate tetrahedral (Q^2), pyrophosphate (Q^1), and other strontium/antimony anions. The occurrences of Q^1 in the crystalline ultraphosphate are due to the disproportionate of the type $2Q^2 \leftrightarrow Q^1+Q^3$ that occurred in these glasses. All the symmetric and asymmetric stretching vibrations of POP and PO_2 observed in the spectra are the characterization of Q^3 and Q^2 groups. Furthermore, the glass network, especially the Q^2 unit can be modified by the SrO and Sb_2O_3 ions. This modification was primarily associated with the phosphate and the Q^2 and Q^3 units that were randomly distributed in the network. Spectroscopic results show that the modification of the phosphate network was higher and more flexible for the glass containing Sb_2O_3 with respect to the SrO. Formations of P-O-H bonds express the hygroscopic nature of the phosphate glass. From this study, it shows that the vibration spectroscopy (Infrared and Raman) are useful complement information about the network structure of the ultraphosphate glasses.

Keywords: strontium antimony phosphate; glass; ultraphosphate; Raman spectroscopy; infrared spectroscopy;

INTRODUCTION

In recent years, glasses are increasingly used as host material for solid state lasers based on rare earth and transition metal ionic transitions [1]. The advantages with glasses are the ease with which large homogeneous pieces can be produced. The nonlinear refractive indices can be made low and the doping concentration can be large [2]. It has been shown that the fluorescence intensity of rare earth ion are enhanced several fold when glass hosts with low phonon energies as example in germinate and telluride are used [2].

Among oxide glasses, phosphate glasses are particularly attractive hosts because they can accommodate large concentrations of active ions without losing the useful properties of the material [3]. Phosphate glasses are relatively easy to prepare and offer an important range of compositional possibilities (ultra, meta, pyro, and orthophosphate), which facilitate tailoring of the physical and chemical properties of interest for specific technological applications [4,5].

Phosphate based glasses have been interest due to their several special properties such as large thermal expansion coefficients, low melting temperatures, solubility, etc. It is also an excellent host material due to good chemical durability, ion exchange ability, high gain coefficient, wide band width capability and low up conversion emission [6,7]. The nonradioactive processes include processes characteristic of the host and processes characteristic of the active ion promoted by its concentration. Phosphate glass present high solubility of rare earth ions allowing a high concentration of active ion into a small volume of the phosphate glass. However, the chemical stability such as hygroscopicity and vitality of phosphate glasses, poses a serious problem for any viable technological application.

EXPERIMENTAL DETAILS

Sample Preparation

Two series of glass samples based on $60P_2O_5$-$x$$Sb_2O_3$-(40-$x$)SrO, (95-$x$)$P_2O_5-5Sb_2O_3$-$x$SrO and (95-$x$)$P_2O_5$-$x$$Sb_2O_3$-5SrO with $5 \leq x \leq 35$ mol% were prepared by melt quenching technique. The batch mixture (20 g) was prepared using raw materials of reagent grade P_2O_5, Sb_2O_3, and SrO. Before the melting process, the powders were mixed and homogenized by milling the powders for 2 hours. The glasses were then melted in porcelain crucible in an electric furnace between 1200 °C – 1300 °C for 15 to 30 minutes depending on composition until clear homogenous melt was obtained. The molten glass was then poured onto a steel plate and press quickly with another steel plate which was subsequently annealed at temperature of 350 °C for 3 hours. The sample then was left to cool inside the furnace at an average rate of 10 °C/min to room temperature.

Characterization

The structure of the glass samples was analyzed using analytical tools such as X-ray diffraction (XRD), FTIR spectroscopy and photoluminescence spectroscopy. The XRD measurements were carried out with CuK_α radiation at room temperature using Siemens Diffractometer D5000, equipped with diffraction software analysis. The infrared (IR) spectra have been recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer from 4000 to 400 cm^{-1} at intervals of 4 cm^{-1}. There were no characteristic absorption bands in the range of 4000 – 1300 cm^{-1} for the samples. Hence the spectra are presented for the region of 1200–400 cm^{-1} in this work. Measurements were carried out on dispersed in pressed KBr pellets containing the same weight of the powder samples to enable us to roughly compare the relative intensities of the bands.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The strontium antimony phosphate glass samples obtained were transparent and showed no sign of devitrification. XRD pattern of the studied glass have shown in Figure 1, that all the samples are completely amorphous which is lacks long-range order according to X-ray diffraction with absence of sharp, strongly peak. The result also showed that the samples do not display any crystalline phase.

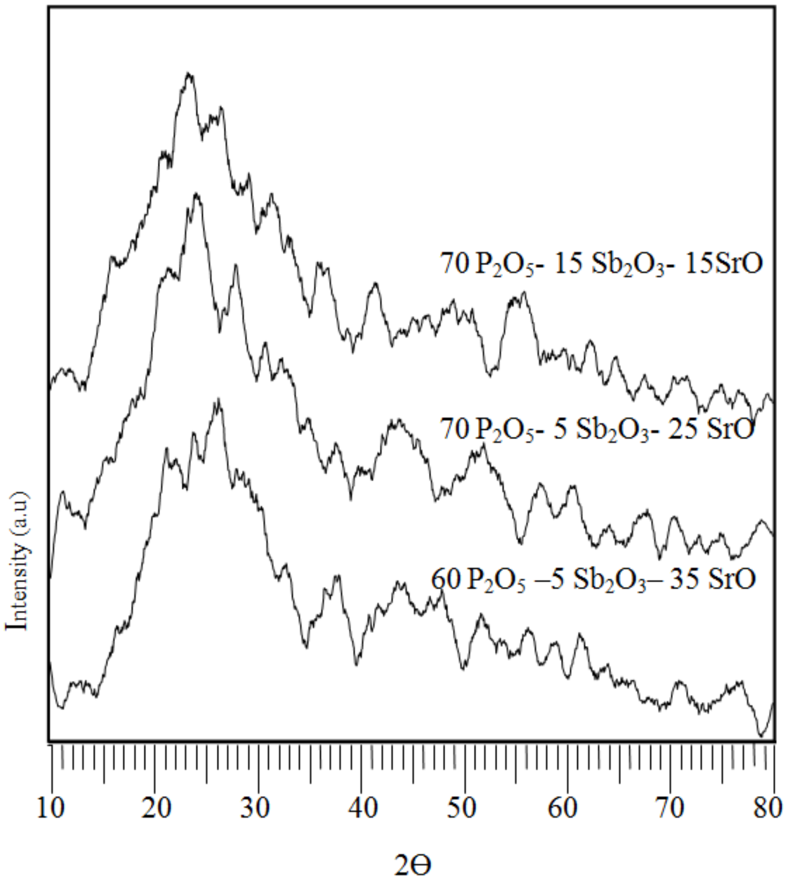

Figure 1: XRD Patterns of the some prepared glasses

Raman Spectra Analysis

Raman spectra of $60P_2O_5$-(40-x) Sb_2O_3-xSrO for a constant P_2O_5 with varies composition of SrO in the range $0 \leq x \leq 35$ mol% are shown in Figure 2(a). The shape of Raman Spectra of the investigated glasses are quite similar and feature a dominant peak at around 1238-1244 cm^{-1} and 1073-1165 cm^{-1}, a shoulder with low intensity around ~987-1023 cm^{-1}, a shoulder at 708-744 cm^{-1}, peak at 573-685 cm^{-1} and a number of bands with weak intensity at ~418-518 cm^{-1} and 302-328 cm^{-1}.

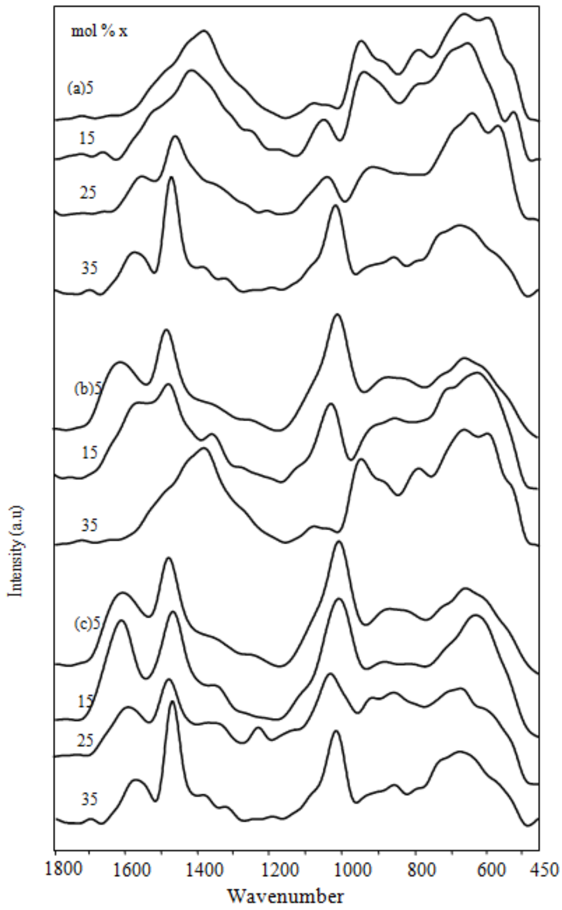

Figure 2: Raman spectra for the composition of (a) 60P_2O_5-(40-x)Sb_2O_3-xSrO (b) (95-x)P_2O_5-$x$$Sb_2O_3$-5SrO (c) (95-$x$)$P_2O_5-5Sb_2O_3$-$x$SrO

The peak around 1238-1244 cm^{-1} is due to the P=O symmetric stretch. Band near 1073-1165 cm^{-1} are due to the symmetric stretch of PO_2 group, i.e stretching motion of the two non bridging oxygen (NBO) atoms bonded to phosphorus atoms (PO_2) in the Q^2 phosphate tetrahedral and those near 995 cm^{-1} are due to the symmetric stretch of PO_2 group [5].

Bands in the frequency region from 573-685 cm^{-1} have been attributed to motions of bridging oxygen in P-O-P chains, originates from the P-O-P symmetric stretch of bridging oxygen in Q^2 species whereas the band at 708-744 cm^{-1} [5], arise from the asymmetric vibrating of the same species. The broad band at 302-328 cm^{-1} has been assigned to bending vibrations of phosphate network/polyhedral δ(POP). New features appear at ~1060 cm^{-1} (when $x \leq 15$) in the spectra of samples with increasing Sb_2O_3 content due to v_s (PO), vibrational of terminal/end groups PO_3 of Q^1 species.

The relative intensity of the P=O band ~ 1238-1244 cm^{-1} the intensity of both asymmetric 1073-1165 cm^{-1} and symmetric 987-1023 cm^{-1} PO_2 band slightly decrease with increasing Sb_2O_3 content. The frequency at P=O, symmetric and asymmetric P-O-P band slightly increase but at asymmetric and symmetric PO_2 band decrease with addition of Sb_2O_3 [6].

Raman spectra of (95-*x*) P_2O_5-*x* Sb_2O_3-5SrO for a constant SrO with composition in the range $0 \leq x \leq 35$ mol% are shown in Figure 2(b). The shape of Raman Spectra of the investigated glasses are quite similar and feature a dominant peak at around 1238-1299 cm^{-1} and 1073-1172 cm^{-1}, a shoulder with low intensity around ~987-1048 cm^{-1}, a shoulder at 752-772 cm^{-1}, peak at 616-688 cm^{-1} and a number of bands with weak intensity at ~441-5541 cm^{-1} and 291-317 cm^{-1}.

The peak around 1238-1299 cm^{-1} is due to the symmetric phosphoryl stretch, (P=O) sym [7]. Band near 1073-1172 cm^{-1} are due to the symmetric stretch of PO_2 group, i.e stretching motion of the two non bridging oxygen (NBO) atoms bonded to phosphorus atoms (PO_2) in the Q^2 phosphate tetrahedral and those near 1000 cm^{-1} are due to the symmetric stretch of PO_2 group. Bands in the frequency region from 616-688 cm^{-1} have been attributed to motions of bridging oxygen in P-O-P chains, originates from the P-O-P symmetric stretch of bridging oxygen in Q^2 species whereas the band at 752-772 cm^{-1}, arise from the asymmetric vibrating of the same species.

The broad band at 291-317 cm^{-1} has been assigned to bending vibrations of phosphate network/polyhedral δ (POP). New features appear at 1060 cm^{-1} and near 742 cm^{-1} in the spectra of samples with increasing Sb_2O_3 content due to $v_s(PO_3)^{2-}$, vibrational of terminal/end groups PO_3 of Q^1 species and v_s(POP), the bridging (POP) oxygen atoms in Q^1 phosphate group. The relative intensity and frequency extremely change for P=O, symmetric and asymmetric PO_2, and symmetric and asymmetric P-O-P band when content of Sb_2O_3 increase.

Raman spectra of (95-*x*) P_2O_5-5Sb_2O_3-*x* SrO for a constant Sb_2O_3 with composition in the range $0 \leq x \leq 35$ mol% are shown in Figure 2(c). The shape of Raman Spectra of the investigated glasses are quite similar and feature a dominant peak at around 1244-1301 cm^{-1} and 1160-1172 cm^{-1}, a shoulder with low intensity around ~999-1160 cm^{-1} a shoulder at 771-774 cm^{-1}, peak at 676-697 cm^{-1} and a number of bands with weak intensity at ~518-550 cm^{-1} and 292-328 cm^{-1}.

The peak around 1244-1301 cm^{-1} is due to the P=O symmetric stretch. Band near 1160-1172 cm^{-1} are due to the symmetric stretch of PO_2 group, i.e stretching motion of the two non bridging oxygen (NBO) atoms bonded to phosphorus atoms (PO_2) in the Q^2 phosphate tetrahedral and those near 1050 cm^{-1} are due to the symmetric stretch of PO_2 group. Bands in the frequency region from 676-697 cm^{-1} have been attributed to motions of bridging oxygen in P-O-P chains, originates from the P-O-P symmetric stretch of bridging oxygen in Q^2 species whereas the band at 771-774 cm^{-1}, arise from the asymmetric vibrating of the same species [8].

The broad band at 292-328 cm^{-1} has been assigned to bending vibrations of phosphate network/polyhedral δ (POP). The relative intensity of the P=O band ~1244-1301 cm^{-1}, the intensity of both asymmetric 1160-1172 cm^{-1} and symmetric 999-1160 cm^{-1} PO_2 band slightly decrease with increasing SrO content [1]. All the frequency of P=O, symmetric and asymmetric P-O-P band slightly increase but at asymmetric and symmetric PO_2 band decrease with addition of Sb_2O_3.

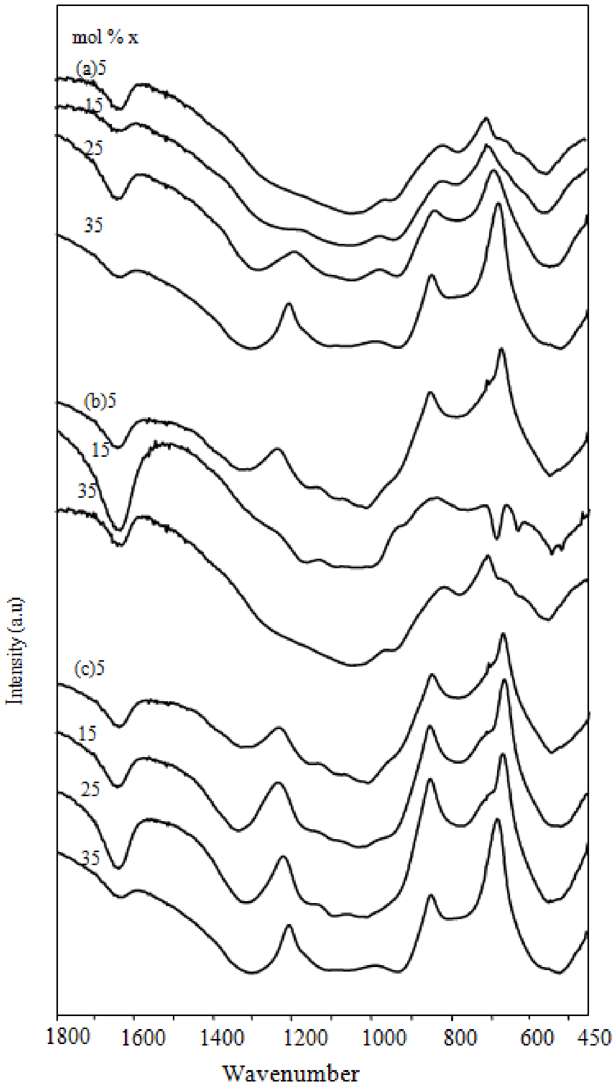

Figure 3: FT-IR spectra for the composition of (a) $60P_2O_5$-(40-x)Sb_2O_3-xSrO b) (95-x)P_2O_5-$x$$Sb_2O_3$-5SrO c) (95-$x$)$P_2O_5-5Sb_2O_3$-$x$SrO

Infrared Spectra Analysis

The infrared spectra of the $60P_2O_5$-(40-x) Sb_2O_3-xSrO, with $5 \leq x \leq 35$ mol% glasses are shown in Figure 3. The typical features of the IR spectrum of the v-P_2O_5 glass are *v*(P=O) bands at 1287 cm^{-1} the asymmetric stretching band, v_{as}(POP) at 895 cm^{-1} and symmetric stretching bands v_s(POP) at 737 cm^{-1}. The bands arising from the vibration of the phosphate glass network appear in the range 1400-500 cm^{-1}.

Three main regions can be distinguished in this range; the region between 1400-1150 cm^{-1} is a characteristic of vibrations of non-bridging PO_2 groups, the region between 1150-900 cm^{-1} is characteristic of terminal P-O (and/or PO_3 groups) and the region between 900-700 cm^{-1} is characteristic of the vibrations of bridging P-O-P groups. All the symmetric and asymmetric stretching vibrations observed in the spectra are characteristic of Q^3, Q^2, and Q^1 groups.

The IR spectra of the (95-*x*) P_2O_5-*x*Sb_2O_3-5SrO glasses are shown in Figure 3(a). The typical features of the IR spectrum of the *v*-P_2O_5 glass are *v*(P=O) bands at 1334-1305 cm^{-1} the asymmetric stretching band, v_{as}(POP) at 887-910 cm^{-1} and symmetric stretching ,bands v_s(POP) at 737 cm^{-1}. The bands arising from the vibration of the phosphate glass network appear in the range 1400-500 cm^{-1}.

Three main regions can be distinguished in this range; the region between 1400-1150 cm^{-1} is a characteristic of vibrations of non-bridging PO_2 groups, the region between 1150-900 cm^{-1} is characteristic of terminal P-O (and/or PO_3 groups) and the region between 900-700 cm^{-1} is characteristic of the vibrations of bridging P-O-P groups. Especially the band at 737-745cm^{-1} originates from the P–O–P symmetric stretch of bridging oxygens in Q^2 species whereas the band at 888-910 cm^{-1} arises from the asymmetric vibrations of the same species [9]. All the symmetric and asymmetric stretching vibrations observed in the spectra are characteristic of Q^3, Q^2 and Q^1 groups.

The IR spectra of the (95-*x*) P_2O_5-5Sb_2O_3-*x*SrO ,glasses are shown in Figure 3(b).The typical IR features of anhydrous P_2O_5 glass are the P=O band at 1287-1319 cm^{-1} and the asymmetric and symmetric P–O–P stretching bands at 899-910 cm^{-1} and 736 -766 cm^{-1},respectively. Glasses with low SrO content have IR features similar to those in the *v*-P_2O_5 spectrum (1378, 930, and 787 cm^{-1}).

The P=O band (1319 cm^{-1}) shifts to lower frequency (1287 cm^{-1}), and its intensity gradually decreases with increasing SrO. The frequency of the asymmetric P–O–P band decreases from 910 to 899 cm^{-1} and the frequency of the symmetric P–O–P band increases from ~745 to 766 cm^{-1} Figure 3(c) shows the IR spectra from several of the (95-*x*) P_2O_5-5Sb_2O_3-*x*SrO glasses.

Peak assignments made in previous studies [9] are used here. The band near 1319 cm^{-1} is due to the P=O symmetric stretch. Bands near 1132 cm^{-1} are due to the asymmetric stretch of PO_2 groups and those near 1075–1029 cm^{-1} are due to the symmetric stretch of PO_2 groups. The bands near 745 and 910 cm^{-1} are due to symmetric and asymmetric stretching of the P–O–P groups respectively. The relative intensity of the P=O band (1319 cm^{-1}) decreases and the intensity of both asymmetric (1132 cm^{-1}) and symmetric

(1075 cm^{-1}) PO_2 bands increase with increasing SrO content. The frequency of the symmetric P–O–P (745 cm^{-1}) band increases and its intensity decreases with the addition of SrO.

CONCLUSION

The IR and Raman spectra suggest that the sample glasses structure has similar structures consisting of randomly distribution of Q^3, Q^2 and Q^1 structural units. The presents of Q^1(pyrophosphate) in the ultraphosphate due to disproportionation of the type $2Q^2 \leftrightarrow Q^1 + Q^3$ occur in these glass. All the symmetric and asymmetric stretching vibrations of POP and PO_2 observed in the spectra are characteristic of Q^3 and Q^2 groups.

Spectroscopic results show that the modification of the phosphate network is higher and more flexible for the Sb_2O_3 containing glass with respect to the SrO. This relationship between composition and the structure can be seen clearly from the result that we obtain. Increasing of Sb_2O_3 modified the phosphate structure extremely as compared to the modification of SrO due to phosphate structure.

XRD pattern of the studied sample showed no sign of devitrification and crystalline phase.

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