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SHORT RANGE STRUCTURE OF SODIUM CALCIUM PHOSPHATE GLASS BY INFRARED AND RAMAN SPECTROSCOPY

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ABSTRACT

The aim of this study is to determine the influence of CaO and Na_2O in the short range structure of metaphosphate composition. Sodium calcium phosphate glasses were prepared using melt quenching technique. The crystallinity of the samples was measured using XRD, while the short range structures were measured by IR and Raman spectroscopy. There is no crystalline phase detected from XRD analysis. This result shows that the prepared samples are glasses. Both IR and Raman results show that the main structure unit presents are composed of Q^2 (middle) and Q^3 (branching) tetrahedral units. The Q^2 units were modified by the presence of Na and Ca ions while the spectrum showed that the P=O become weaken with the increasing of Na content. The spectral shifted to lower frequency at the asymmetric vibration (O-P-O) as Na_2O is replaced by CaO. The asymmetric stretching band of (P-O-P) shifted to higher frequency with the substitution of CaO for Na_2O. It is obviously show that the addition of modifier of CaO and Na_2O changed the structure features of metaphosphate glass composition.

Keywords: Phosphate glass; Infrared Spectroscopy; Raman spectroscopy; XRD; metaphosphate;

INTRODUCTION

Glasses are increasingly used as host material for solid state lasers based on rare earth and transition metal ionic transitions. 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. 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 tellurite are used [1, 2].

In recent years, phosphate based glasses have attracted a lot of interest due to their several special properties such as large thermal expansion coefficients, low melting temperatures, solubility, etc. [3, 4]. It is also an excellent host material due to good chemical durability, ion exchange ability, high gain coefficient, wide band width capability and low upconversion emission. The nonradiative 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 [5]. 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. 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 [6, 7].

The basic structural units of crystalline and amorphous phosphates are the PO_4 tetrahedral and these tetrahedral links through covalent bridging oxygen to form various phosphate anions [8-11]. These tetrahedral are classified using the Qn terminology, where n represents the number of bridging oxygen per tetrahedron [12, 13]. The networks of phosphate glasses can be classified by the oxygento-phosphorus ratio, which sets the number of tetrahedral linkages, through bridging oxygen, between neighboring P-tetrahedral. Phosphate glasses can be made with a range of structures, from a cross-linked network of Q^3 tetrahedral (vitreous v-P_2O_5) to polymer-like metaphosphate chains of Q^2 tetrahedral to pyro- (Q^1) and orthophosphate (Q^0) anions, depending on the modifier composition as shown schematically in Figure 1.

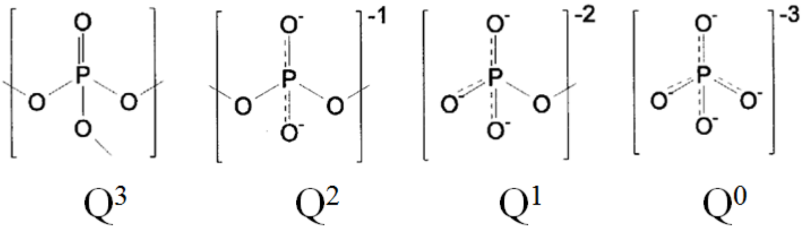

Figure 1: The Q^n tetrahedral

Spectroscopy (IR and Raman) has been used as an important tool to study the nature of glasses for the past many years. The relative impact of spectroscopy has probably been greater in the analysis of glasses than those of crystals. Galeener and Mikkelsen [14] reported the first Raman spectra from anhydrous v-P_2O_5. Due to the P_2O_5 is hygroscopic and volatile, anhydrous glasses have been prepared using dry-box handling procedures from crystalline P_2O_5 and then melted in sealed silica ampoules.

The understanding of the glasses structure on different length scales remains difficult mainly due to the lack of periodicity inherent to glasses. Only the suitable correlation of experimental data obtained from several investigations provided by different methods allows the finding of helpful structural information. The use of complementary techniques such as Raman, infrared (IR) and NMR spectroscopy has proven to be an efficient examination way of the glasses structure, in general and of the phosphate glasses structure, in particular.

In this study, basic composition of xNa_2O-(50-x)CaO $50P_2O_5$, 10NaO-(90-x)CaO-xP_2O_5, (80-x)Na_2O-20CaO-xP_2O_5 (all the compositions are referred to mol %), are chosen as host base glass. The aim of the present work is to investigate the complementary information about the local order around phosphorus tetrahedral structures due to the incorporation of mix alkali earth cation (Ca and Na) oxide to ultraphosphates network using both Fourier-transformed infrared (FT-IR) and Raman spectroscopy.

EXPERIMENTAL METHOD

Sample Preparation

A three series of sodium calcium phosphate glasses with compositions of series I; xNa_2O-(50-x)CaO-$50P_2O_5$, series II; 10NaO-(90-x)CaO-xP_2O_5 and series III; (80-x)Na_2O-20CaO-xP_2O_5 where $0.4 \leq x \leq 0.6$ are prepared using melt quenching technique. Reagent-grade H_3PO_4 (85% liquid), Na_2O, and CaO were used as the starting materials. The corresponding weights of the starting materials were mixed thoroughly in platinum crucible and placed in air in an electric furnace. The melted glass was pour onto a metal plate and annealed for 3 hours at 300 ^oC. The furnace was then switch off and the sample was left out until it cooled at room temperature before being removed from the furnace.

Characterization

The structure of the prepared samples was analyzed using analytical tools such as X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy. The XRD measurements were carried out with CuK_α radiation operating at 40 kV, 30 mA with Bragg-Brentano geometry at room temperature using Siemens Diffractometer D5000, equipped with diffraction software analysis. The diffraction patterns were collected at constant (2θ) steps of 0.04^o, where 2θ from 20° to 80^o, and dwell of 4 s.

The infrared (IR) spectra had 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 were observed in the region 1200-400 cm^{-1} for this work. Measurements were carried out using KBr pellets method. This method is containing the same weight ratio of the powder samples in order to compare the relative intensities of the IR bands.

The Raman spectra were measured with a Perkin-Elmer Spectrum GX spectrometer in the spectral range 100–4000 cm^{-1}. The sample was excited with an argon ion laser with power of about 200 mW. The spectrum was observed in the quasi-back scattered mode. The digital intensity data were recorded at intervals of 4 cm^{-1} and the spectral resolution was about 4 cm^{-1}.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

The sodium calcium phosphate glass samples obtained were transparent and showed no sign of diversification. The XRD patterns of (80-x)Na_2O-20CaO-xP_2O_5 glasses with $0.4 \le x \le 0.6$ are shown in Figure 2. These results indicated that all the obtained samples were fully amorphous and do not present any crystalline phase.

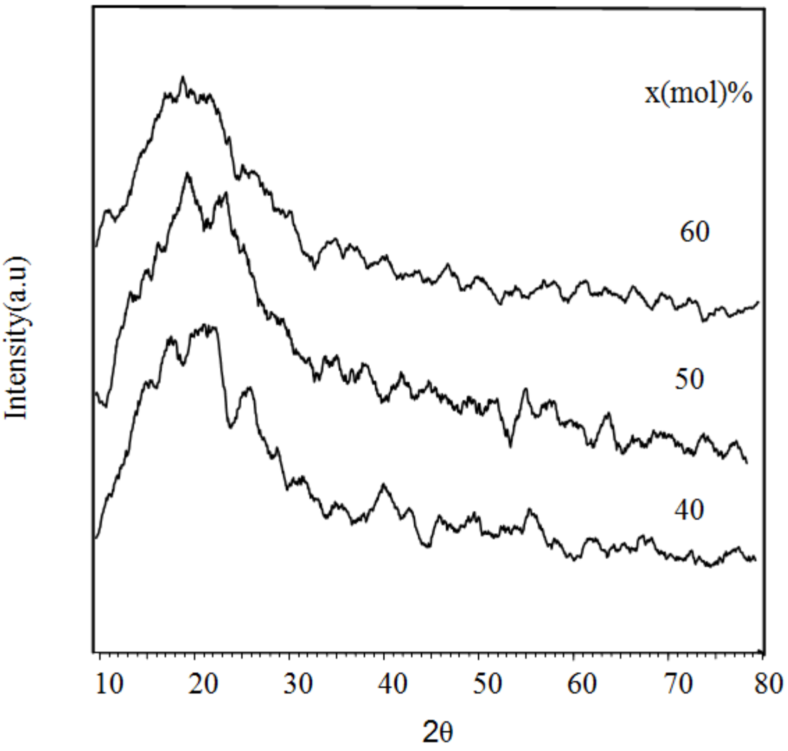

Figure 2: XRD patterns for some of (80-x)Na_2O-20CaO-xP_2O_5 glasses with $0.4 \le x \le 0.6$

Infrared Spectra Analysis

The infrared spectra of series I with different criteria of 10Na_2O-40CaO-50P_2O_5, 25Na_2O-25CaO-50P_2O_5 and 30Na_2O-20CaO-50P_2O_5 glasses are shows in Figure 3 (a). The band assignment is shown in Table 1. The strong band observed at 1340 cm^{-1} is assigned to the characteristic stretching mode of the P=O bond. The band is obviously become smaller (x=50), indicating a decrease in the double bond character and the effective force constant of the (P=O) bonds with increasing the Na content.

The band near 1278 cm^{-1} is assigned to asymmetric stretching mode of the two non bridging oxygen atoms bonded to phosphorus atoms, the O-P-O or (PO_2)as units in the phosphate tetrahedral. These bands shift to lower frequency and their amplitude decreases as Na_2O replaced by CaO because the calcium-oxygen bond is more covalent than the sodium-oxygen bond. This result indicates that the phosphate linkages are shortened as incorporate into the glass structure and leading to increase the relative content of the Q^2 units.

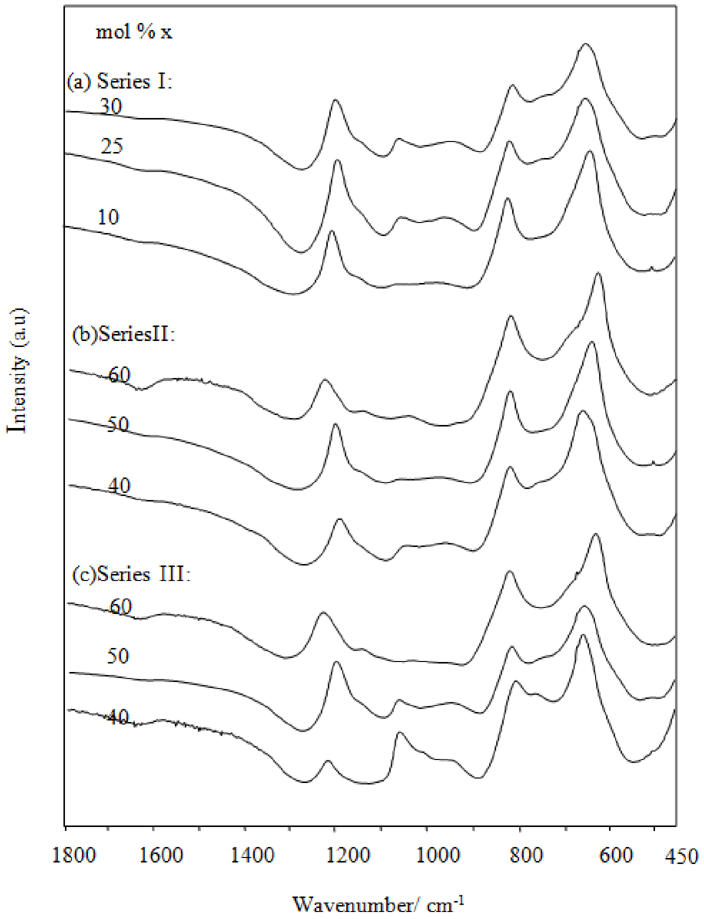

Figure 3: FT-IR spectra for the composition of (a) xNa_2O-(50-x)CaO- $50P_2O_5$ (b) 10NaO- (90-x)CaO-xP_2O_5 (c) (80-x)Na_2O-20CaO-xP_2O_5

The absorption of P-O$^-$ group near 1100 cm^{-1} obviously shift to lower frequency as CaO replaces Na_2O. The absorptions band near 895 cm^{-1} is assigned to the asymmetric stretching mode of the P-O-P linkages, while two modes around 752 and 776 cm^{-1} are attributed to *vs*(P-O-P) the asymmetric stretching of the bridging oxygen atoms bonded to a phosphorus atom in a Q^2 phosphate as reported by Husin [15]. The asymmetric stretching band of P-O-P shifts to higher frequency as the Na_2O is increased from 10 up to 30 % mol as reported by Husin [15].

Figure 3 (b) and (c) shows infrared spectra series II with composes of $10Na_2O$-(90-x)CaO-xP_2O_5 and series III 20CaO-(80-x)Na_2O-xP_2O_5. The glasses are contains of 10% mol Na_2O for series II and 20% mol of CaO for series III. All the symmetric and asymmetric stretching vibrations are observed in the spectra are almost similar as series I. The only difference is the intensity of each spectrum. For series II, the band at 1160

cm^{-1} for the (PO_2) symmetry intensity at (x=50) are higher than other bands. Also, the difference in intensity can be seen at band 773 to 780 cm^{-1} for asymmetry stretching P-O-P. The intensity is changing because of the changes on Q^2 and Q^3 units. For series III, the changes in intensity can be seen at the band 770 cm^{-1} for v(PO). The intensity decreasing as the amount of CaO is decrease.

Table 1: FTIR spectra band assignment

Series	x	v_sPOP	v_{as}POP	vPO	V_sPO$_2$	v_{as}PO$_2$	(P=O)$_s$
I	10	776	878	1087	1185	1290	1338
Constant	25	752	894	1099	1184	1278	1322
P_2O_5	30	773	895	1097	1180	1279	1340
II	60	623	779	984	1086	1160	1279
Constant	50	639	773	980	1087	1164	1289
NaO	40	647	780	975	1089	1157	1278
III	60	771	919	1095	1093	1315	1341
Constant	50	774	879	1100	1175	1280	1347
CaO	40	773	884	1095	1169	1271	1336

Raman Spectra Analysis

Figure 4 (a) shows the Raman spectra of series I; (50-x)CaO-xNa_2O-50P_2O_5 and the band assignment is shown in Table 2. The shape of Raman spectra of the investigated glasses are similar and feature a dominant peak at around 1330 cm^{-1} and 1176 cm^{-1}, a peak with low intensity around ~1050 cm^{-1}, a shoulder at 786 cm^{-1}, and peaks at ~694 cm^{-1}.

The peaks around 1320 cm^{-1} is due to the P=O symmetric stretch. Bands near 1170 cm^{-1} are due to the asymmetric stretch of PO_2 groups, i.e stretching motions 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 groups.

The bands in the frequency region from 687 to 694 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, the band at 771-786 cm^{-1} arises from the asymmetric vibrations of the same species whereas the band in the frequencies region from 909-982 cm^{-1} have attributed to motions of P-O groups.

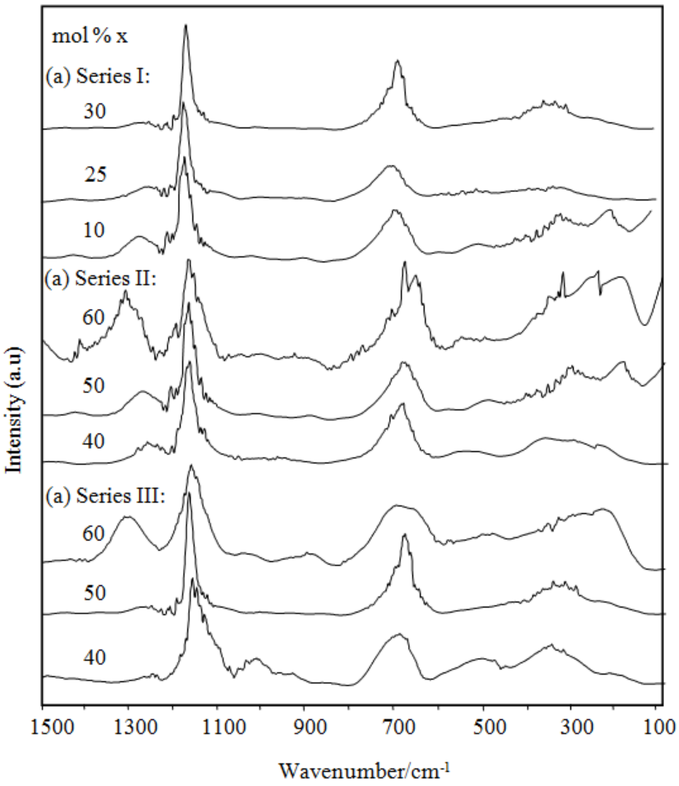

Figure 4: Raman spectra of different composition (a) xNa_2O-(50-x)CaO- 50P_2O_5 (b) 10NaO-(90-x)CaO-xP_2O_5 (c) (80-x)Na_2O-20CaO-xP_2O_5

The results have shown that the phosphate glass structure in the metaphosphate composition as example in the series I consists of a main network of a chain composed of Q^2 tetrahedral units, where two of the oxygen atoms are bridging (P-O-P) and two are non-bridging (PO_2). When CaO and Na_2O are added to this group of metaphosphate chains, only little change occurred as it revealed from the Raman spectra. The intensity at double bond slightly decreases with increasing Na_2O and CaO content.

Figure 3(b) and (c) shows Raman spectra of series II; (90-x)CaO-10Na_2O-xP_2O_5 and series III; (80-x)Na_2O-20CaO-xP_2O_5. The glasses containing 10% mol Na_2O for series II while 20% mol CaO for series III. All the symmetric and asymmetric stretching vibrations observed in the spectra are similar as series I. However, for series II, the main difference intensity is at band 690 cm^{-1}. The intensity of the spectrum increase when P_2O_5 is increase due to the decreasing of CaO content. The strongest band observed at (x=60) 1314 cm^{-1} is assigned to the characteristics stretching mode of the P=O bond as the amount of P_2O_5 is high and the contents of Na_2O and CaO are small. For series III, the peak at band 690 cm^{-1} *vs*(POP) is sharp at (x=50) whereas the broad peak can be observed at (x=40) and (x=60). This is due some crystal part that contain in the glass sample of (x=50) were detected by Raman spectroscopy.

Table 2: Raman band assignment

Series	x	v_sPOP	v_{as}POP	vPO	V$_s$PO$_2$	v_{as}PO$_2$	(P=O)$_s$
I	10	694	780	909	1047	1176	1318
Constant	25	693	786	907	1041	1172	1339
P_2O_5	30	687	771	982	1048	1170	1327
II	30	682	778	993	1007	1172	1314
Constant	40	683	772	937	1012	1172	1312
NaO	50	692	778	930	1012	1171	1316
III	20	695	823	978	1077	1166	1316
Constant	30	685	825	976	1083	1170	1314
CaO	40	696	827	973	1080	1164	1315

CONCLUSION

A series of glasses based on ternary diagram with composition of xNa_2O-(50-x)CaO-$50P_2O_5$, 10NaO-(90-x)CaO-xP_2O_5 and (80-x)Na_2O-20CaO-xP_2O_5 were successfully prepared using melt quenching technique. The samples show that all of them are in amorphous state. The intensities of IR and Raman increase with increasing of Na_2O and CaO. The investigated glasses have the similar structures consisting of randomly distribution of Q^2 and Q^3 structural units as observed by IR and Raman spectroscopy. The addition of calcium oxide and sodium oxide give gradual changes of the phosphate glass structure features from a three-dimensional random network to long or very short contains of PO_4 tetrahedral.

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