



Raman spectroscopy of copper phosphate glasses

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Received 4 April 1996; revised 18 November 1996

Abstract

Raman spectra of binary copper phosphate glass samples, $x\text{CuO} \cdot (1-x)\text{P}_2\text{O}_5$, having $x = 0.4, 0.5$, and 0.55 and various $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$ ratios have been measured. The Raman spectra of the samples changed with changing $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$ ratio as well as CuO content. The smaller ionic size and the greater charge of the Cu^{2+} ion than those of the Cu^{1+} ion create larger in-chain P–O–P bond angles and smaller out-of-chain PO_2 angle as well as greater Cu–O field strength. Differing local structures of Cu^{1+} and Cu^{2+} ions in phosphate glass results in a variation of Raman spectra of the glasses depending on the $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$ ratio. Also, a decrease in phosphate chain length with increasing CuO content affected the Raman spectra of the glasses. Although the crystallization of the samples is not detected in the X-ray diffraction, the overlapping bands in the Raman spectra of the 0.55 CuO samples are attributed to crystalline phases.

PACS: 78.30; 61.43.F; 63.50

1. Introduction

Phosphate glasses are of technological interest due to their several unique properties, such as high thermal expansion coefficient, low viscosity resulting in low melting and softening temperatures, UV transmission and other optical properties, and electrical conduction [1]. The technological importance of these glasses requires a detailed understanding of the molecular and structural chemistry in order for glasses to be designed for particular applications.

Raman scattering spectra have been used for investigation of the molecular structure of phosphate

glasses [2–10]. In the Raman spectra of metaphosphate glasses, there are bands at $\sim 695 \text{ cm}^{-1}$ for the $\nu_s(\text{POP})$ vibration, at $\sim 1173 \text{ cm}^{-1}$ for the $\nu_s(\text{PO}_2)$ vibration, and a band at $\sim 1270 \text{ cm}^{-1}$ for the $\nu_{\text{as}}(\text{PO}_2)$ vibration. The position and shape of these bands have been found to be sensitive to the phosphate chain length and the network modifier species.

Recently, simple binary copper phosphate glasses having various $[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$ (will be called $[\text{Cu}^{2+}]$ ratio) were prepared and it was shown that the crystallization behavior, optical absorption and chemical durability of the glasses were affected by this ratio [11–16]. It was observed that the reduced copper phosphate glass had a lower softening temperature and an improved chemical durability than those of the oxidized glass [14]. These changes in the properties of the glasses depending on the $[\text{Cu}^{2+}]$

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ratio is due to a variation of glass structure. However, effects of $[\text{Cu}^{2+}]$ ratio on the structure of copper phosphate glasses cannot be observed in infrared spectroscopy nor in nuclear magnetic resonance (NMR) spectra [16]. Changes in depolymerization of phosphate chain as a function of the $[\text{Cu}^{2+}]$ ratio were not observed in XPS analysis of copper phosphate glasses [16].

The Raman spectra of rare-earth phosphate glasses were not affected by their redox state [3]. In this study, Raman scattering spectra of binary copper phosphate glasses having different $[\text{Cu}^{2+}]$ ratios and glass compositions were measured. Thus, we investigated the variation of molecular structure of copper phosphate glasses as a function of the $[\text{Cu}^{2+}]$ ratio and glass composition.

2. Experimental

2.1. Glass preparation

$\text{CuO-P}_2\text{O}_5$ glass samples having compositions, $x\text{CuO} \cdot (1-x)\text{P}_2\text{O}_5$, with $x = 0.4, 0.5,$ and 0.55 were prepared using analytical reagent grades of CuO and $\text{NH}_4\text{H}_2\text{PO}_4$. Samples with different oxidation state ratios of copper were made by using various melting times as described before [11]. About 60 g of chemicals were mixed with isopropyl alcohol and dried to obtain homogenized batches. A quartz crucible (100 ml capacity) containing the batch was heated initially at 500°C for about 2 h in order to evaporate ammonia and water in the batch and minimize the tendency for subsequent phosphate loss. A quartz crucible was used since it was found that a quartz crucible was more inert to copper phosphate liquid

than an alumina crucible [11]. The crucible was transferred to another furnace, which was preheated to the melting temperature, 1000°C . The batch was melted in air from 15 min to 6 h depending on the desired oxidation state ratio of copper in glass. The liquid was poured onto a clean copper plate and cast into a disc shape of 3 mm thickness. The samples were annealed for 5 h at 200°C to 500°C depending on their $[\text{Cu}^{2+}]$ ratio. The samples are listed in Table 1 with their melting and annealing conditions. All the samples were stored in a vacuum desiccator to prevent reaction with moisture in air.

2.2. Analysis

The powdered glasses were confirmed to be amorphous using X-ray diffraction (XRD, Rigaku D/MAX-RC) analysis. The concentrations of the total copper and Cu^{2+} in the glasses were determined using complexometric titration described before [11]. The $[\text{Cu}^{2+}]$ ratios of the glasses were calculated and with error range are listed in Table 1.

2.3. Raman spectroscopy

Polished samples were used for measurement of micro-Raman spectroscopy. A schematic diagram for the micro-Raman spectroscopy is shown in Fig. 1. An Ar ion laser (Spectra-Physics 2060-7S Beam Lok) at the wavelength of 488 nm was used for sample excitation. The scattered light was collected through a collecting lens and focused on the slit of a double monochromator (Jobin-Yvon U-1000) whose focal length is 1 m. The monochromatized photon was detected by a photomultiplier tube (Hamamatsu R943-02) which can be cooled to -20°C . The sam-

Table 1
Preparation and chemical analyses of copper phosphate glasses

Glass	Batch composition	Melting temperature ($^\circ\text{C}$)	Melting time	Annealing temperature ($^\circ\text{C}$)	$[\text{Cu}^{2+}]/[\text{Cu}_{\text{total}}]$ (%)
A	$50\text{Cu} \cdot 50\text{P}_2\text{O}_5$	1000	15 min	200	22 ± 6
C	$50\text{Cu} \cdot 50\text{P}_2\text{O}_5$	1000	1 hr	300	74 ± 3
E	$50\text{Cu} \cdot 50\text{P}_2\text{O}_5$	1000	6 h	500	99 ± 1
F	$40\text{Cu} \cdot 60\text{P}_2\text{O}_5$	1000	30 min	200	49 ± 4
G	$40\text{Cu} \cdot 60\text{P}_2\text{O}_5$	1000	6 h	500	100 ± 1
H	$55\text{Cu} \cdot 45\text{P}_2\text{O}_5$	1000	30 min	200	56 ± 4
I	$55\text{Cu} \cdot 45\text{P}_2\text{O}_5$	1000	6 h	400	82 ± 3

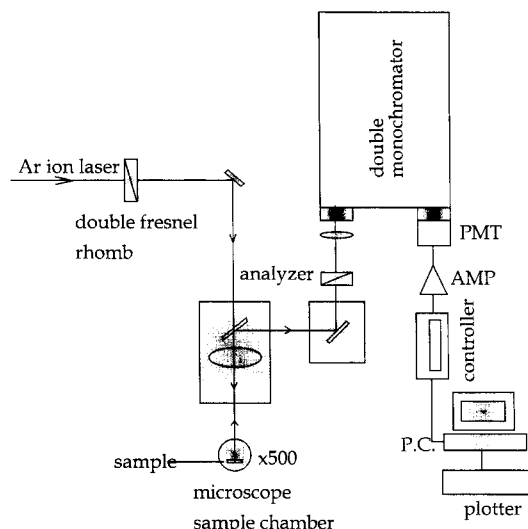


Fig. 1. Schematic diagram for the micro-Raman spectroscopy

ple was mounted on the specimen holder of a microscope whose magnification was $\times 500$. Power of the laser at the sample was typically ~ 350 mW. Spectra of the samples were taken in the frequency region between 200 and 1500 cm^{-1} at a spectral bandpass of 1 cm^{-1} .

3. Results

Raman spectra in the frequency region between 200 and 1500 cm^{-1} of the samples having a nominal composition $0.5\text{CuO} \cdot 0.5\text{P}_2\text{O}_5$ and different $[\text{Cu}^{2+}]$ ratios are shown in Fig. 2. These spectra are characteristic of binary phosphate glasses [2–10]. Two frequency regions in the Raman spectra contain information about the structure of the phosphate glasses. The bands in the frequency region between 600 and 850 cm^{-1} bands are vibrations of the in-chain P–O–P stretch. The bands in the frequency region between 950 and 1400 cm^{-1} bands are vibrations of out-of-chain $-\text{PO}_2^{2-}$ stretch. In the frequency region of POP vibration, a main band near 700 cm^{-1} and a shoulder at $\sim 800\text{ cm}^{-1}$ are observed. The main band near 700 cm^{-1} increases in frequency from 703 cm^{-1} to 714 cm^{-1} as the $[\text{Cu}^{2+}]$ ratio increases. In the frequency region of PO_2 vibration, a band near 1200 cm^{-1} and shoulders at larger and

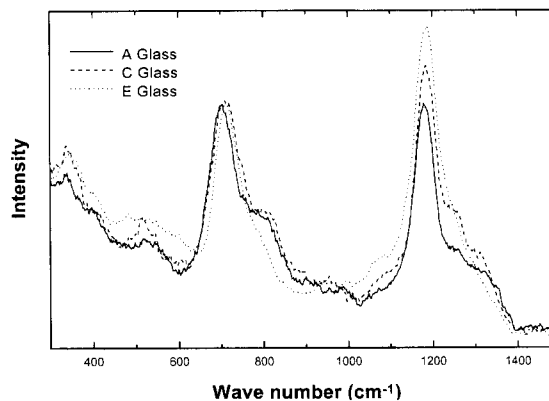


Fig. 2. Raman spectra of copper phosphate glasses having a nominal composition $50\text{CuO} \cdot 50\text{P}_2\text{O}_5$.

smaller wavenumbers are observed. As the $[\text{Cu}^{2+}]$ ratio decreases, the shoulder on the smaller wavenumber side is diminished and the shoulder on the larger wavenumber side increased. Also, the wavenumber and the width of the main band around 1200 cm^{-1} changed with increasing $[\text{Cu}^{2+}]$ ratio. Comparing the two main bands at 700 cm^{-1} and 1200 cm^{-1} , the intensity of the band at 1200 cm^{-1} grows with increasing $[\text{Cu}^{2+}]$ ratio. In addition to the main regions of the bands, broad and scattered overlapping bands near 300 and 500 cm^{-1} are observed.

Fig. 3 shows the Raman spectra of the reduced and oxidized samples having a nominal composition $0.4\text{CuO} \cdot 0.6\text{P}_2\text{O}_5$. As in the spectra of the 0.5CuO samples, the main bands around 700 cm^{-1} and 1200 cm^{-1} are present, and the position of the band

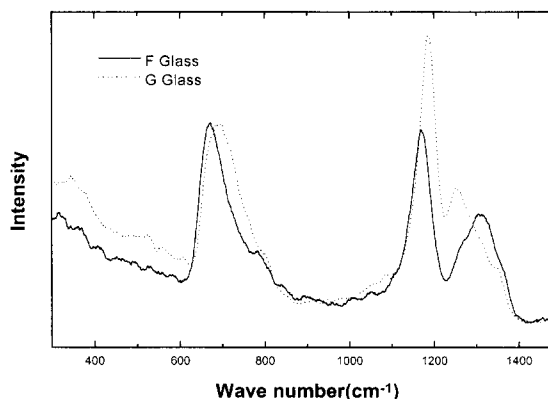


Fig. 3. Raman spectra of copper phosphate glasses having a nominal composition $40\text{CuO} \cdot 60\text{P}_2\text{O}_5$.

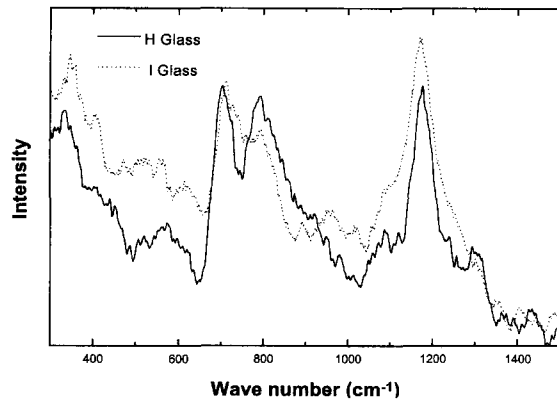


Fig. 4. Raman spectra of copper phosphate glasses having a nominal composition $55\text{CuO} \cdot 45\text{P}_2\text{O}_5$.

moves to larger wavenumber in the oxidized sample. The relative intensity of the band near 1200 cm^{-1} to that of the band near 700 cm^{-1} is greater for the oxidized sample as shown in the spectra of the 0.5CuO samples. Also, there are shoulders at about 800 cm^{-1} and 1100 cm^{-1} in the main bands and broad bands in the wavenumber range between 300 cm^{-1} and 600 cm^{-1} . In addition to two main bands, another sharp band around 1300 cm^{-1} which is not obvious for in the spectrum of the 0.5CuO sample is observed in the spectra of the 0.4CuO sample. The wavenumber of the band shifts from 1254 cm^{-1} in spectrum of the oxidized glass to 1311 cm^{-1} in the spectrum of the reduced sample.

The Raman spectra of the reduced and oxidized samples having a nominal composition $0.55\text{CuO} \cdot 0.45\text{P}_2\text{O}_5$ are presented in Fig. 4. Two distinct frequency regions and two main bands are present as in the spectra of the samples having other compositions. Also, the bands around 800 cm^{-1} and 900 cm^{-1} are observed. However, the other bands are not resolved.

4. Discussion

The assignments of the bands in the Raman spectra of binary phosphate glasses have been discussed in the literature [2–10]. Usually, the Raman spectrum of the metaphosphate glass has two bands in the frequency region of the in-chain POP vibration and

several bands in the frequency region of the out-of-chain PO_2 vibration. These bands have been fit to asymmetric profiles deduced from the asymmetric distribution of bonding schemes in phosphate glasses [10]. The main band position and the relative intensity ratio of these bands for the samples are listed in Table 2. The asymmetric band at 700 cm^{-1} is assigned to the symmetric stretch of in-chain POP vibration in the long-chain phosphate species. It has been previously observed in similar phosphate glasses that this band increases in frequency as the chain length decreases [6,10]. The shift in the frequency of the band is attributed to a change in the in-chain P–O–P bond angle depending on the effect of the network modifier on phosphate glass structure [4,5]. The larger wavenumber of the band is a result of the smaller P–O–P bond angle which results from shorter phosphate chain length or smaller metal cation size. The phosphate chain length of the glasses having larger CuO content is shorter due to the depolymerization of phosphate structure. Thus, the position of the band shifts to larger wavenumber with increasing CuO content as listed in Table 2. This shift of the $\nu_s(\text{POP})$ band to larger wavenumber with increasing metal oxide content has been observed in other binary phosphate glasses [3,6,9,10]. Also, the larger wavenumber of the $\nu_s(\text{POP})$ band for the larger $[\text{Cu}^{2+}]$ ratio glass can be attributed to shorter phosphate chain length of the glass. The phosphate chain length can decrease as Cu^{2+} ions replace Cu^{1+} ions in phosphate glass, as expected in mixed alkali and alkaline earth phosphate glasses [17]. However, the variations of Raman spectra depending on the $[\text{Cu}^{2+}]$ ratio are not always consistent with the variations

Table 2

Wavenumbers and relative amplitude ratios of the bands in the Raman spectra of copper phosphate glasses

Glass	$\nu_s(\text{POP})$ $\pm 2\text{ (cm}^{-1}\text{)}$	$\nu_s(\text{PO}_2)$ $\pm 2\text{ (cm}^{-1}\text{)}$	$I[\nu_s(\text{PO}_2)]/I[\nu_s(\text{POP})]$ ± 0.04
A	703	1180	1.00
C	710	1185	1.15
E	714	1188	1.33
F	672	1170	0.97
G	698	1187	1.44
H	701	1171	1.00
I	711	1171	1.16

with phosphate chain length that have been observed in other phosphate glasses [3,6,9,10]. For example, the relative intensity ratio, $I[\nu_s(\text{PO}_2)]/I[\nu_s(\text{POP})]$, which increases with increasing $[\text{Cu}^{2+}]$ ratio as shown in Table 2, should decrease with the depolymerization of phosphate structure as observed in calcium phosphate glasses [10]. In addition, changes in phosphate chain length as a function of $[\text{Cu}^{2+}]$ ratio was not found in XPS analysis of copper phosphate glasses [16]. Thus, we expect that phosphate chain length does not change but local bonding changes depend on the $[\text{Cu}^{2+}]$ ratio in copper phosphate glasses. Therefore, the shift in the wavenumber of the band is due to the different ionic size of Cu^{1+} and Cu^{2+} rather than a change in phosphate chain length. The smaller ionic size of Cu^{2+} compared to Cu^{1+} results in a smaller P–O–P bond angle causing the shift of the band to longer frequency in the spectrum of the larger $[\text{Cu}^{2+}]$ ratio sample.

A second $\nu_s(\text{POP})$ band near 800 cm^{-1} which existed as a shoulder on the main band has been observed but not assigned [6]. However, it was hypothesized that this band may be due to very short phosphate chain units or ring structures that are known to be increasingly important in the composition region between the ultraphosphate and metaphosphate compositions [17].

Several bands have been observed in the region of the spectrum containing out-of-chain PO_2 vibration. Two main bands at 1180 cm^{-1} and 1270 cm^{-1} in this region are present in the spectra of metaphosphate glasses and assigned to the symmetric stretch and asymmetric stretch of PO_2 vibrations, respectively. The change in the wavenumber and width of the bands depending on the kind and concentration of network modifiers in phosphate glasses has been investigated and reported [4,5]. Rouse et al. [5] calculated the dependence of the $\nu_s(\text{PO}_2)$ and $\nu_{as}(\text{PO}_2)$ bands on two parameters (metal–oxygen bond force constant and average PO_2 angle) using a simple vibrational model in mixed alkali metaphosphate glasses. As the metal–oxygen bond force constant increases and the average PO_2 angle decreases, the $\nu_s(\text{PO}_2)$ band increases in frequency. The increase in the frequency of the $\nu_s(\text{PO}_2)$ band as phosphate chain length is shortened, indicative of a decrease in the average PO_2 angle, has been observed in other phosphate glasses [3,6,9,10,18]. However, a consis-

tent variation in the frequency of the $\nu_s(\text{PO}_2)$ band with changing CuO content in copper phosphate glasses is not observed since the effect of metal cation is larger. As Cu^{2+} ions replace Cu^{1+} ions in the phosphate glass structure, the greater Cu–O bond force constant and the smaller average PO_2 angle is obtained because of the greater field strength of the Cu^{2+} ion compared to that of the Cu^{1+} ion. Thus, the $\nu_s(\text{PO}_2)$ band shifts to larger wavenumber due to both the greater Cu–O bond force constant and the smaller average PO_2 angle with increase of the $[\text{Cu}^{2+}]$ ratio in the glass.

In addition, the $\nu_s(\text{PO}_2)$ band intensity is sensitive to the degree of covalency in the P–O bond [5,7,10]. The greater electronegativity of Cu^{1+} ion has an effect of making the P–O bond more ionic than does the Cu^{2+} ion because it increases the charge separation between the negative oxygen and the positive phosphorous by withdrawing electrons from P–O bond. Thus, as shown in Table 2, the relative $\nu_s(\text{PO}_2)$ band intensity is increased with increasing $[\text{Cu}^{2+}]$ ratio since the P–O bond has a larger covalent fraction. Also, the relative $\nu_s(\text{PO}_2)$ band intensity is reduced with increasing CuO content for the glasses having similar $[\text{Cu}^{2+}]$ ratio as already found in calcium phosphate glasses [10].

The most notable change in the Raman spectra in binary phosphate glasses is the decrease in $\nu_{as}(\text{PO}_2)$ band near 1270 cm^{-1} with increasing CuO concentration. This change is characteristic of phosphate glasses and consistent with depolymerization of the three dimensional networks. Thus, a distinct and small width $\nu_{as}(\text{PO}_2)$ band is observed in the 0.4CuO samples but is uncertain in the 0.5 and 0.55 CuO samples. However, a change in the intensity of $\nu_{as}(\text{PO}_2)$ band is not observed in the spectra of the oxidized and reduced samples with 0.4CuO composition since we assume that the phosphate chain length does not change with variation of the $[\text{Cu}^{2+}]$ ratio. On the other hand, the change of the $\nu_{as}(\text{PO}_2)$ band in frequency from 1254 cm^{-1} to 1311 cm^{-1} is observed in the spectra of oxidized and reduced samples. Based on the calculation of Rouse et al. [5], the wavenumber of the $\nu_{as}(\text{PO}_2)$ band increases with decreasing field strength of cation and increasing average PO_2 angle. Thus, the lower frequency of the $\nu_{as}(\text{PO}_2)$ band for the larger $[\text{Cu}^{2+}]$ ratio is due to both the greater field strength and the smaller aver-

age PO_2 angle produced by the smaller ionic size of Cu^{2+} compared to that of Cu^{1+} .

In addition to two main bands, bands at 1022, 1134 and 1350 cm^{-1} are observed in phosphate glasses. The bands at 1022 and 1350 cm^{-1} have been assigned to the $\nu_s(\text{PO}_3^{2-})$ vibration and the residual P=O double bond vibration, respectively. However, these bands are not resolved and their assignments are unknown. For the 0.5CuO sample, the P=O band is not detected or moves to smaller frequency and the amplitude of the $\nu_s(\text{PO}_3^{2-})$ band increases with increasing $[\text{Cu}^{2+}]$ ratio. This increase indicates that the structure of localized P=O bond is disentangled to have terminal PO_3^{2-} groups as the $[\text{Cu}^{2+}]$ ratio increases [19].

For the 0.55CuO sample, band at 800 cm^{-1} and band broadening in the spectral range of 800 to 1100 cm^{-1} and below 600 cm^{-1} , which have not been observed in other binary phosphate glasses, are present. Recently, similar Raman spectra in calcium phosphate glasses was reported [10]. These bands in the spectra were attributed to crystallization of the glasses although evidence for the presence of crystalline phases was not observed in the XRD data. The broad bands at 738 cm^{-1} and 780 cm^{-1} in the spectra of calcium phosphate glasses are assigned to the crystalline phases of γ - and α - $\text{Ca}_2\text{P}_2\text{O}_7$ respectively, as are numerous bands in the spectra of the crystalline $\text{Ca}_2\text{P}_2\text{O}_7$ phases in the region of the PO_2 vibrations [10]. Bands for α - $\text{Ca}_2\text{P}_2\text{O}_7$ crystalline phase were observed at 1005, 1072, 1102, 1162 and 1208 cm^{-1} [10]. Bands from a γ - $\text{Ca}_2\text{P}_2\text{O}_7$ crystalline phase were observed at 1046 and 1134 cm^{-1} in this region. Thus, we make similar Raman spectral assignments of copper phosphate crystalline phases in copper phosphate glasses. The broad bands are composed of the bands for crystalline phases although all the glasses are confirmed to be amorphous in the XRD result shown in Fig. 5. This interpretation of these bands may indicate that crystallization of the glasses which is not detected in XRD can be found in the Raman spectrum. The numerous crystalline bands are too broad to be resolved.

For all the glasses, the broad overlapping bands are observed in the wavenumber region between 300 and 600 cm^{-1} . Their assignment is not unambiguous because these bands are due to complicated internal vibrations such as the skeletal deformation vibration

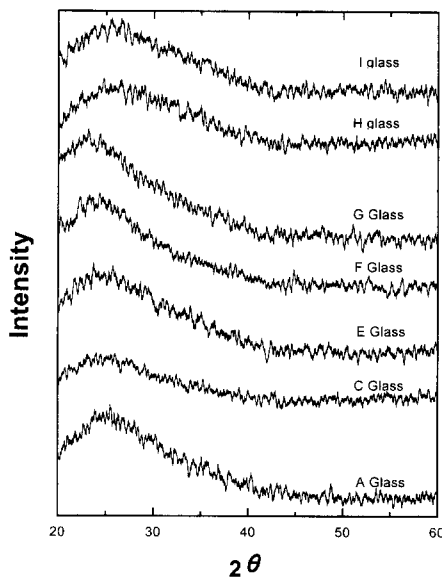


Fig. 5. XRD results for copper phosphate glasses.

of phosphate chains and PO_3 deformation vibrations of pyrophosphate segments [3,19].

5. Conclusions

The Raman spectroscopy of copper phosphate glasses is affected by the $[\text{Cu}^{2+}]$ ratio as well as CuO content in the glass. The decrease in phosphate chain length with increasing CuO content in the glass has a effect on the Raman spectra of copper phosphate glasses. The frequency of $\nu_s(\text{POP})$ band is smaller and the $\nu_{as}(\text{PO}_2)$ band is observed in the spectra of the sample containing smallest CuO content because of the shorter phosphate chain length as observed in other phosphate glasses. However, the change in Raman spectra as a function of the $[\text{Cu}^{2+}]$ ratio is attributed to the differing size and charge of Cu^{1+} and Cu^{2+} rather than to depolymerization of phosphate chain. As the $[\text{Cu}^{2+}]$ ratio increases, both $\nu_s(\text{POP})$ and $\nu_s(\text{PO}_2)$ bands shift to larger wavenumbers due to the greater field strength of Cu^{2+} ion and the relative peak intensity of $\nu_s(\text{PO}_2)$ band to $\nu_s(\text{POP})$ band increases due to increasing covalency of the P–O bond. Evidence for crystallization of 0.55CuO sample is found in the Raman spectrum although it is not detected in the XRD.

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