Digest Journal of Nanomaterials and Biostructures Vol. 11, No. 2, April – June 2016, p. 607 - 614

RAMAN AND UV-VIS-NIR SPECTROSCOPY OF PHOSPHATE GLASSES

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Phosphate glasses with compositions (70-x) P_2O_5- 30ZnO- xCuO (where x= 10, 15 and 20 in mol%) have been prepared by melt-quenching Procedure. Effect of CuO percentage on the density of prepared samples has been studied. It was found that density decreases from 2.923 to 2.653 $gm{\cdot}cm^{-3}$ when CuO increases from 10 to 20 mol%. The values of molar volume (V_m), oxygen packing density (O. P. d), oxygen molar volume (V_O), optical energy gap (E_{opt}) and glass transition temperature (T_g) of prepared glasses ware estimated. Moreover the UV-Vis-NIR spectroscopic study has been done and the optical properties of the prepared glasses were estimated. The optical band gap energy (E_{opt}) has been calculated, it was observed that E_{opt} increases from 3.33 eV to 3.43 eV with increasing CuO content from 10 to 20 mol%. Herein the glass system 60 P_2O_5- 30ZnO- 10CuO has two cut off wavelengths firstly at 420 nm and secondly at 1665 nm while the glasses modified by 15 and 20 mol% of CuO have only one cutoff wavelength in NIR region. The prepared glasses have transmission broad band from 1665 to 2940 nm. The structure of this glasses investigated by using Raman spectra. The optical properties results indicated that the prepared glasses are promising for optical filter applications in visible, NIR and IR region.

(Received April 11, 2016; Accepted June 4, 2016)

Keywords: Phosphate glasses*;* Optical properties; bandpass filter, Raman.

1. Introduction

Recently, phosphate based glasses (PBGs) doped with different cations which act as network modifiers can be used for many applications. Specialty Glasses embedding monovalent ions like Ag^+ and Li^+ can be used in ionic conductor solid state laser and nonlinear optics. Cu^{2+} doped phosphate glasses exhibited unique optical properties. Furthermore, PBGs containing trivalent rare earth ions (Re^{3+}) showed magnetic and luminescence behavior. Moreover, Ag^+ and Cu^+ ions have been added to PBGs and estimated for their potential antimicrobial properties [1- 3]. The tetrahedral PO_4^{3-} ions are the basic building blocks for phosphate glasses [1], which can be crosslinked using different modifiers cations. The Chemical stability of PBGs was significantly improved through embedding modifiers like ZnO. The Zn ions serve as anionic cross linker between different phosphate anions, hindering the hydration process [4]. Also the doping of Cu into PBGs is expected to improve their physico-chemical characteristics. The copper doped phosphate glasses are of great interest due to their good electrical and optical characteristics. Some of the important applications of Cu doped PBGs include; heat absorbers, superionic conductors, solid state lasers, nonlinear optical devices in addition to copper releasing degradable phosphate glass fibres, which have potential uses in wound healing or as plant fertilizers [5, 6]. Besides, the Cu doped PBGs showed an optical absorption peak in the visible light band [7- 9]. The present

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research study focused on the effect of simultaneous incorporation of Cu and Zn in phosphate glasses. An extended UV-Vis-NIR spectroscopic study has been performed. The experimental results suggested that, the prepared glasses with copper can be potentially applicable as optical band pass filter.

2. Experimental Work

The glasses were prepared by the conventional quenching procedure. First; 50 g of the compositions; $60P_2O_5$ –30ZnO- 10CuO in mol% (sample A), $55P_2O_5$ – 30ZnO- 15CuO in mol% (sample B) and $50P_2O_5$ – 30ZnO- 20CuO in mol% (sample C) have been melted in alumina crucibles, the temperature was probably between1000 and1100 °C. Composites were cast in a steel mold at room temperature followed by annealing at 400 °C for 2 h. After annealing, the furnace was turned off and the samples were left to cool down inside. Before testing, the prepared glasses were finely polished. The bulk density has been determined by using gas pycnometer (Model: UltraPyc 1200e).

X-ray diffraction spectroscopy has been performed by using, (Schimadzu Labx XRD-6000) using CuK_α radiation at 40 kV,2θ between 5 to 90°.

The calorimetric measurements of prepared glasses were carried out in Setaram (DSC 131 Evo). Temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and melting enthalpies of high purity indium and zinc. For non-isothermal experiments, the prepared sample (10 mg) was sealed in an aluminum pan and it tempered at 15 K/min. An empty aluminum pan was used as reference and in all cases flow of nitrogen was maintained at 60 ml/min in order to extract the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC 131 Evo furnace**.**

The absorbance and transmittance were measured by using UV-VIS-NIR double beam spectrophotometer (Model: UV – 3600, Japan),the wavelength range was 190-3200 nm.

The vertical (VV) polarized spontaneous Raman spectra of the prepared glass were acquired using a Thermo Scientific DXR Raman Microscope spectroscopy setup with 532 nm excitation [(532 nm Laser type Diode-pumped, solid state (DPSS)] and acquisition time was set to 30 seconds. The incoming signal vertically surface of the bulk sample, and V-polarized Raman scattered signal was collected in the backscattering geometry with a 100x microscope objective.

3. Result and discussion

Homogeneous glasses were prepared in the glass system $60P_2O_5$ – 30ZnO- 10CuO in mol% (sample A), $55P_2O_5$ – 30ZnO- 15CuO in mol% (sample B) and $50P_2O_5$ – 30ZnO- 20CuO in mol% (sample C) respectively. The color of prepared samples had changed depending on the ratio of CuO in the composition. They have been altered from transparent green to slightly dark green with increasing CuO from 10 to 20 mol%. The change in color of the prepared glass samples may be due to the copper ions optical absorption caused by electronic transitions within d orbital. Copper, has a $(3d)^9$ electronic configuration in the ground state, when Cu+ ions replace the host cation providing a larger ionic radius i.e. occupy off- centered sites in the ground state. This color is generally observed when transition ions have been doped in the metaphosphate glasses, so we can use these composites in optical devices.

XRD patterns of the prepared samples are introduced in Fig.1. As it is clear, no sharp peaks were identified instead a broad diffraction peak has been obtained which denotes the amorphous nature of prepared samples.The density, ρ, of prepared glass samples has been decreased from 2.923 to 2.653 in g· cm^{-3} as the CuO content increased from 10 to 20mol% this is due to the replacement of P_2O_5 by CuO which is of less molar mass. The phosphate pentaoxide (P_2O_5) is heavier of molecular weight, M, of the copper oxide this leading to more dense glass matrix. So the density value increases with increasing the P_2O_5concentration and otherwise decrease with increasing CuO concentration in the prepared glasses. We can determinethe molar volume, V_m, by using the relation; $V_m = \frac{M}{\rho}$, and the oxygen molar volume, V_o, is estimated by$V_O =$

$\frac{\sum M x_i}{\rho \cdot \sum x_i n_i}$ where, n_i, is the number of oxygen atoms in each oxide and x_i is the molar fraction of each component, i,. The oxygen packing density, Opd, calculated by this formula ,$Opd = \frac{100 \rho O_i}{M_i}$, where O_i is number of oxygen atoms in the oxide formula. These results of V_m, V_O, and Opd give information about the structure of the prepared glasses. The values of V_m and V_O increase from 40.2 to 41.95 and 11.83 to 13.98 cm^3 with increasing CuO content in mol% from 10 to 20 mol%. Otherwise the value of Opd decreases from 84.55 to 71.51 in g atom lit^{-3} with increasing CuO concentration. Fig. 2 shows the DSC trace of the prepared glasses (sample A), (sample B) and (sample C) at heating rate of $15^0C\cdot min^{-1}$.The addition of CuO to binary glasses P_2O_5- ZnO from 10 to 20mol% results in a regular decrease of T_g from 380 to 363^0C at $15^0C\cdot min^{-1}$. Generally the glass transition is referee to the thermal stability of structural network of prepared glassed. Herein the decreasing of T_g can be interpreted as decreasing of the rigidity of the glass matrix and also with decreasing Opd. Hence the cross link density of the network for the prepared glasses decreased with increasing CuO. Moreover the decrease in T_g indicates that the network structure is becoming more weakness due to the substitution of P_2O_5 by CuO in$(70-x)P_2O_5\cdot 30ZnO\cdot xCuO$ (x=10, 15 and 20) glasses. By addition, the decrease in T_g can be attributed to decrease in the density of prepared glasses with the increase of the copper content. All these data of ρ, V_m, V_O, Opd and T_g were summarized in Table (1).

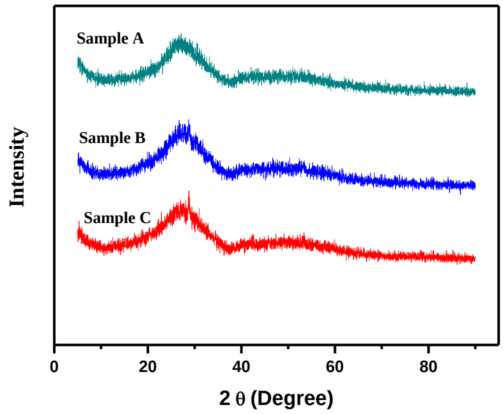

Fig. 1: XRD patterns of the prepared glass samples

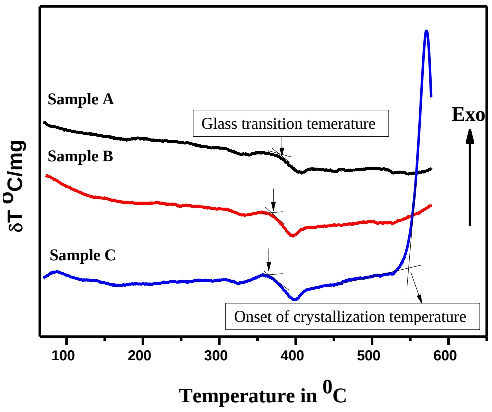

Fig. 2: DSC trace of prepared glasses.

Table (1): Composition, density (ρ), molar volume (V_m), oxygen packing density (O. P. d), oxygen molar volume, optical energy gap (E_{opt}), and glass transition temperature.

Sample code	Composition	Density, ρ (g/cm^{-3})	Molar volume V_M (cm^3)	O. P. d $g.atom.l^{-1}$	Oxygen molar volume, V_o(cm^3)	Optical energy gap (E_{opt}) in eV	Glass transition temperature (^0C)
Sample 1	$60P_2O_5$- 30ZnO- 10CuO	2.923	40.212	84.551	11.827	33.3	380
Sample 2	$55P_2O_5$- 30ZnO- 15CuO	2.798	40.894	78.252	12.779	3.37	369
Sample 3	$50P_2O_5$- 30ZnO- 20CuO	2.653	41.952	71.51	13.984	3.43	363

Fig.3a. shows the UV-Vis-NIR optical transmission spectra of (1-x) P_2O_5- 30ZnO- xCuO with different CuO content ranging from 10 up to 20 mol%. The cut off in the visible band has appeared at 420 nm and another broad band starts in IR ~ 1665 to 2940 nm have been obtained in the glass with composition $60P_2O_5$ – 30ZnO- 10CuO.Approximately the same the broad band appeared glasses composition$55P_2O_5$ – 30ZnO- 15CuO and $50P_2O_5$ – 30ZnO- 20CuO, this is shown in Fig. 3b.But the intensity of transmission increased with increasing CuO content. The broad band of optical absorption spectra from ~ 1625 to 2970 nm have been appeared of the prepared glasses this shown in Fig. 4. So based on the our experimental data we can say that the prepared glasses are promising as used in optical band pass filters in Vis, NIR and IR regions. With increasing the CuO content, the optical absorption band onset is shifted to a lower wavelength has observed for both sample B and sample C glasses where the band onset has been reduced from 1790 to 1625 nm. The observed band shift may be due to the conversion of bridging oxygen to non bridging oxygen (NBO).When addition of copper leads to broading band due to splitting of "d" orbitals which increasing the electron density of the inner shells and enhances the intensitities of bands (see fig. 3a). The obtained absorption bands are most due to the presence of Cu^+ and Cu^{2+} leads in the prepared glasses reduce to the possibility of lasing properties. The bandpass center λ_{max}, FWHM and the area-related to the transmitted energy are the most important parameters which identify the characteristics of bandpass filters. Table (2) summarizes the variations of these parameters with composition. The center of peaks for the developed samples reveal their performance in the NIR band with near attached to IR band i.e. tailoring the developed filters for specific applications. The integration and the peak analysis of prepared glasses were shown in Fig. 5a –c. D. R. Rayan et. al[9]showed that the glasses with composition CuO- BaO-ZnO-NaO-P_2O_5appeared phenomenon of band stop in UV bands. The same phenomenon are observed in various glasses [10 -12]. Otherwise our glass with composition $60P_2O_5$- 30ZnO-10CuO can be use in both UV, IR bands. The incorporation of different concentration of CuO from 10 to 20 mol% to binary glasses P_2O_5- ZnO is assumed to modification the glass network structure and creation IR band due to the field strengths of the network former (P_2O_5) and intermediate ions (ZnO), which confirmed splitting of low symmetry ligand field component.

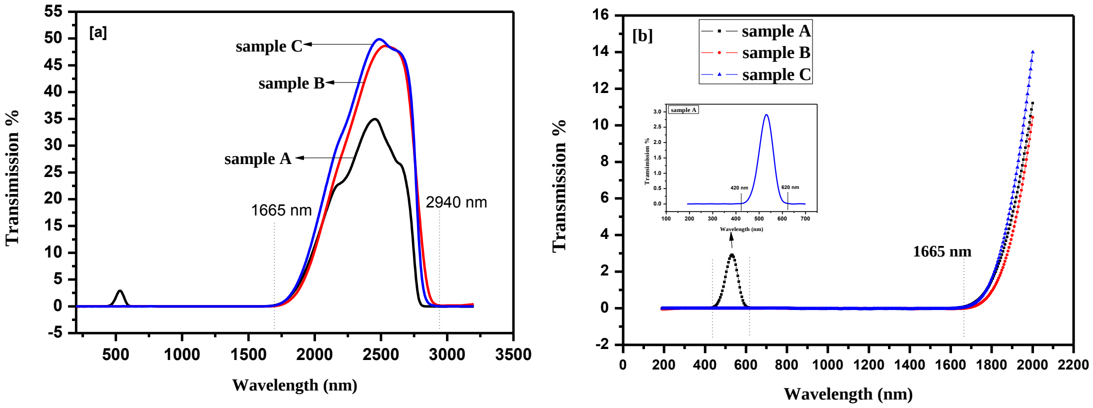

Fig. 3[a]The transmission versus wavelength of the developed glass samples.
[b] The Vis and NIR cut off wavelengths of the developed glass samples.

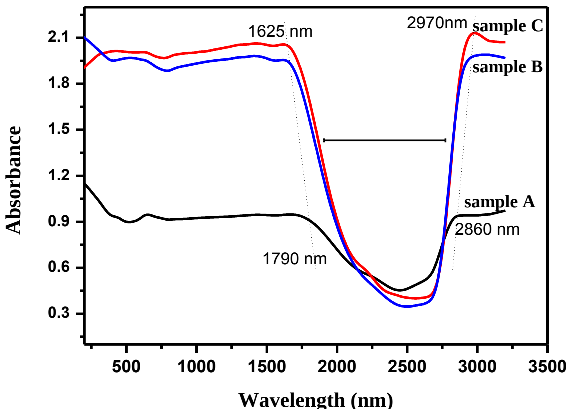

Fig. 4: UV-Vis-NIR absorbance spectra of the developed glass systems

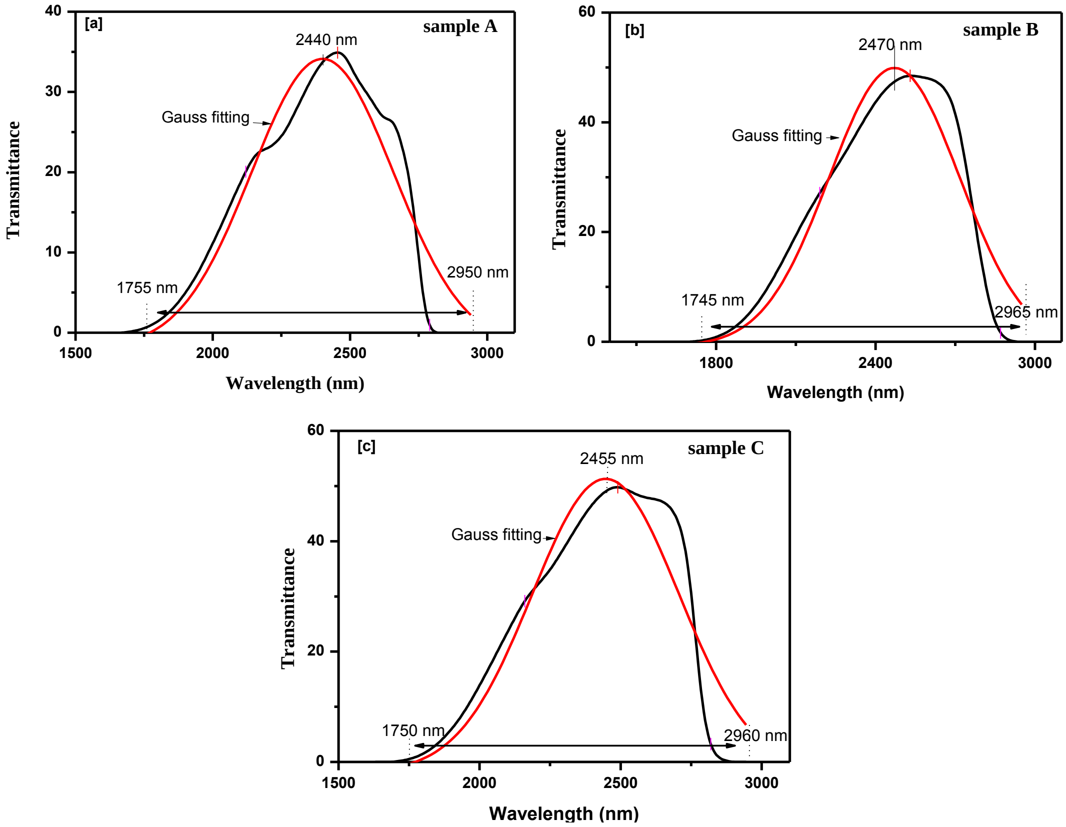

Fig. 5[a]: Gauss fitting, integration, center peak of sample A. [b]: Gauss fitting, integration, center peak of sample B. [c]: Gauss fitting, integration, center peak of sample C.

Table (2): The center maximum wavelength width, λ_{max}, area and full width half maximum FWHM of NIR bandpass region filter of prepared glasses.

Sample code	λ_{max} in nm	Width in nm	Area	FWHM
Sample A	2440	1195	20413	609
Sample B	2470	1220	29361	578
Sample C	2455	1210	31290	613

The optical absorption coefficient $\alpha(\nu)$ can be determined at various wavelengths according to the relation [13];

$$\alpha(\nu) = \frac{1}{d}\ln\left(\frac{I_0}{I}\right) = 2.303\left(\frac{A}{d}\right) \tag{1}$$

Where, ν, is the frequency of radiation, I_0 and I_t stands for intensities of the incident and transmitted light rays, respectively and , *d*, is the thickness of the glass samples. The factor ln(I_0/I) corresponds to absorbance.

Close to the band edge in an amorphous semiconductor, The absorption coefficient, $\alpha(\nu)$, obvious an exponential dependence on, $h\nu$, so Urbach relation can be show as follow; [13],

$$\alpha(\nu) = C\exp(h\nu/\Delta E) \tag{2}$$

Where, C, is a constant, ΔE, corresponding to the width of the tail for the localized states in the band gap. Herein Urbach energies have been determined by taking the reciprocals of slopes of the ln α(ν) *vs.* hνas shown in Fig.6.

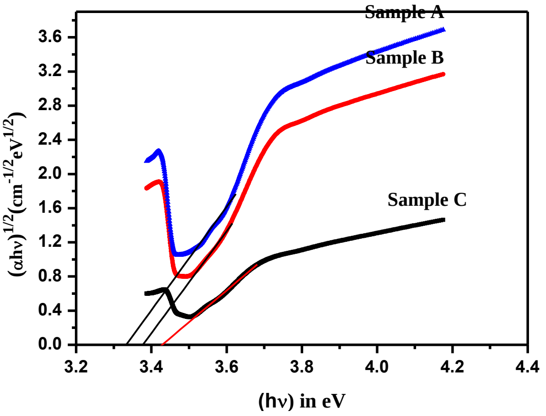

Fig. 6: $(\alpha h\nu)^{1/2}$ *vis.* $h\nu$ *of the developed glass systems.*

From these results, the glass with composition $60P_2O_5$ – 30ZnO- 20CuO has a maximum value of, ΔE, (= 0.1 eV) while that with composition $60P_2O_5$ – 30ZnO- 10CuO has a minimum value ΔE (= 0.04 eV). These values are in considering able conformity with those mentioned for inorganic glass systems [13]. Mott and Davis [14] linked these data to E_g, by the following usual equation considered for amorphous composites;

$$\alpha(\nu) = \frac{\beta(h\nu - E_g)^n}{h\nu} \tag{3}$$

β is a constant and n, taken equal 2 as indirect transition was assumed. Fig.6, shows diagram of $(\alpha h\nu)^{1/2}$*vis.* (hν) for the various CuO contents. E_g was calculated utilizing the linear part of plot by extrapolating it to intercept the hνaxis at $(\alpha h\nu)^{1/2} = 0$. As it is clear E_g has been increased from 3.33 to 3.43 eV as the CuO content increased from 10 to 20 mol%. Some authors [15- 17] have suggested that the changing of the absorption band to lower energy corresponds related to converting the non-bridging oxygen NBO, which has a less-tightly bound electron than bridging oxygen BO. So the decreasing in the energy gap of sample A is caused by increasing in number of NBO. The NBO cause an increase in the degree of localization of electrons thereby increasing the donor center in the glass matrix.

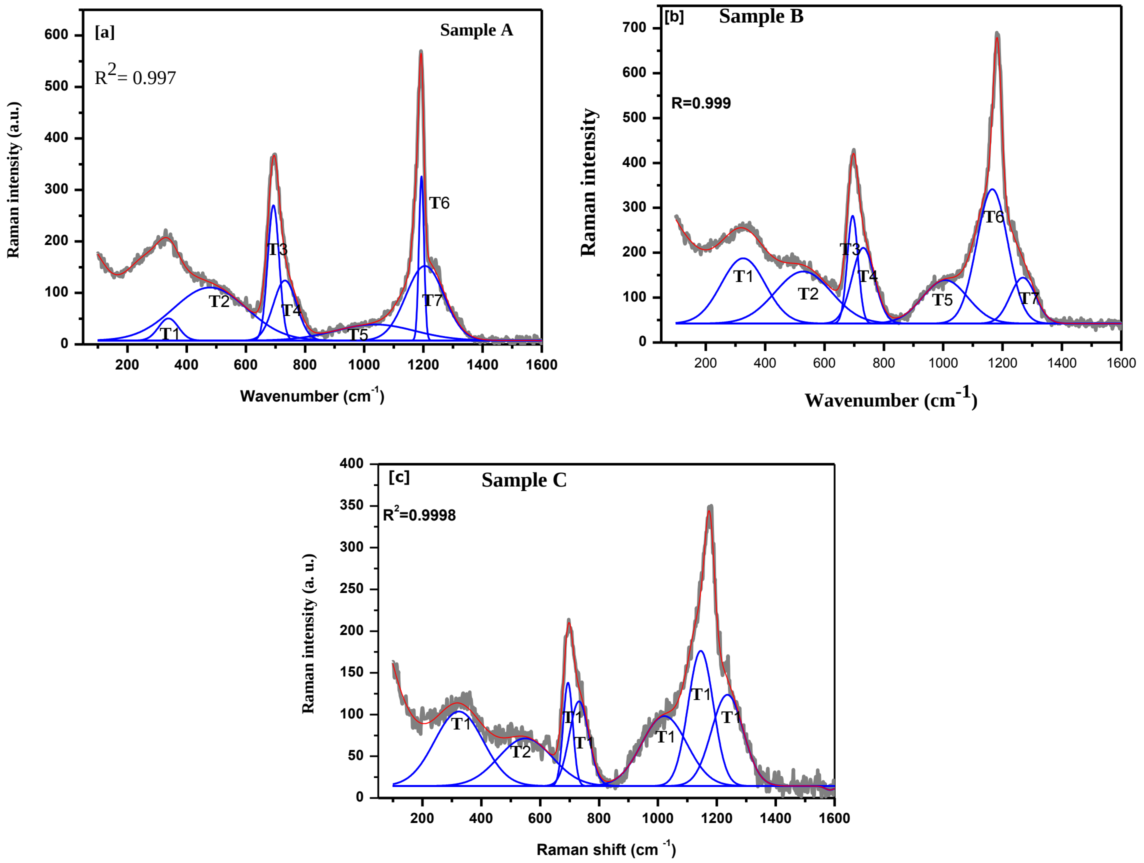

Fig. 7[a]: Deconvolution of Raman spectra of sample A.[b]: Deconvolution Of Raman spectra of sample B.[c]: Deconvolution of Raman spectra of sample C.

Table (3): Peak position of Raman spectra for prepared glasses.

Sample Code	Peak position at cm^{-1}						
	T1	T2	T3	T4	T5	T6	T7
Sample A	339	479	693	732	1036	1193	1205
Sample B	329	529	695	731	1006	1165	1268
Sample C	323	549	694	731	1021	1145	1235

Fig. 7a, b and c shows the Raman spectra and deconvolution of normalized Raman spectra of sample A, sample B and sample C respectively. The structure of these glasses investigated as; the band labeled (T1) around at 323- 339 cm^{-1}can be contributed to P- O- Zn linkages. The band as labeled (T2) around 479- 549 cm^{-1} can be corresponding to the PO_4^{3-}related to P- O- Cu^{2+} bonds [18,19]. A band labeled (T3) around 693-695 cm^{-1}assigned to the symmetric bridging stretching vibration (ν_s) of the –P-O-P- units along the chains [18- 20]. A band labeled (T4) at 731 cm^{-1} can be due to the second symmetric stretching mode of P-O-P bridging bonds in short phosphate units. A band labeled (T5) around 1006- 1036 cm^{-1} observed in pyrophosphates is due to $P2O_7^{4-}$ ions. The band labeled (T6) around 1145- 1193 cm^{-1} can be attributed to the terminal P-O stretching vibrations of the PO_2 units [21- 23]. Finally the band labeled (T7) around 1205- 1268 cm^{-1}related to the P= O, double bond in the polyphosphate chain.

4. Conclusion

Doping CuO into the matrix of P_2O_5/ ZnO binary glass system resulted in constitutional modifications of the glass network providing prepared glasses with unique optical characteristics. The density and T_g of the developed glass systems decrease with increasing CuO content otherwise the optical energy gap E_g increase with increasing CuO concentration. These glasses may be used as bandpass filters in NIR region. Furthermore, glasses with composition $60P_2O_5$ – 30ZnO- 10CuO have been found to be suitable for both UV and NIR bandpass filters. Glass with the composition $60P_2O_5$ – 30ZnO- 15CuO have the highestλ_{max} and NIR band width. The optical transmission and absorption reveals that of these glasses acts as abroad band pass filter in the IR region

Acknowledgments

Authors are thankful to the Deanship of Scientific Research at Princess Nourah Bint Abdualrahman University (PNU) for funding this research project Number (36-S-101).

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