Addition of Cu₂O on Structural and Optical Properties of Alkali Alkali -Earth Zinc Phosphate Glass.

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The structure of $42\%P_2O_5$ - 40%ZnO- 2%CaO- (16-x) $\%Na_2O-xCu_2O$ glasses (x=2, 4, 6, 8, 10%mol) were prepared by conventional melt-quenching technique. The amorphous state of samples was verified by XRD. Density and molar volume were determined. The structural features of the glasses are determined using IR spectroscopy. Obtained data reveal that the density ρ and molar volume M_v depend nonlinearly on composition. The formation of meta, pyro and orthophosphate is in consistent with the results of molar volume, i.e., depends on chemical composition. Obtained optical absorption spectra reveal the presence both of Cu¹⁺ and Cu²⁺ ions in the investigated glasses. A single broad peak observed in the optical spectra which is due to ${}^2A_{1g} \rightarrow {}^2B_{1g}$, ${}^2B_{2g} \rightarrow {}^2B_{1g}$ and ${}^2Eg \rightarrow {}^2B_{1g}$ transition in the distorted octahedral symmetry (elongated).

1. Introduction

Incorporation of the copper into phosphate glasses can give interesting electrical and optical properties that make them suitable for use as super-ionic conductor, solid state laser, color filter and non-linear optics. The main advantage of phosphate glass over other oxide glasses (eg. silicate and borate) is its ability to accommodate high concentration of transition metals and remain amorphous [1-3]. In addition, phosphate glasses enjoy a range of compositional and structural possibilities (ultra, meta, pyro and ortho) that facilitate tailoring chemical and physical properties of interest for specific technological applications. PO₄ tetrahedra are the basic structural unit in phosphate glass. These tetrahedral units are described by the Qⁿ notion where 'n' represents the number of bridging oxygen (BO's) that link neighboring P-tetrahedra. Vitreous P_2O_5 structure has Q³ P-tetrahedra with three BO's and one double bonded oxygen P=O, forming a three-dimensional cross-linked network. Ultraphosphate glasses have both Q³ and Q² P-tetrahedral structural units. Metaphosphate

glasses have Q^2 units has two NBO's, which are usually assumed to be different since the first terminal oxygen is bounded by P=O, while the other terminal oxygen forms P-O⁻ bond. The Q² tetrahedra link to form long chains (or rings). Phosphate glasses based on pyro Q¹ and orthophosphate Q⁰ units are also possible [4-6, 7].

Generally doped-copper glass can exist in multi valence state Cu^{2+} ions, monovalent Cu^+ ions and metallic copper (Cu^0) although most glasses melted under ordinary atmospheric conditions are usually assumed that they do not contain metallic copper. Colors produced by Cu^{1+}/Cu^{2+} ions have been investigated and interpreted from the view of ligand field theory. The octahedral coordination of Cu^{1+}/Cu^{2+} ion in the glass produces a ligand field which produces splitting of the free ion energy level. The absorption band is a result of energy transition between these perturbed energy level. The optical single absorption band of Cu^{1+} in phosphate glasses is centered in the UV region but their tails are extending into the visible region. While Cu^{2+} has optical absorption bands in the visible-near infrared region of the spectrum [8-14].

In the present work, the structural and optical properties of $42P_2O_5$ -40ZnO-2CaO- (16-x) Na₂O- xCu₂O glasses, where x=2, 4, 6, 8, 10% (in mole %), respectively, have been investigated.

2-Expermintal:

Copper-doped glasses of varying basic hosts including zinc sodium calcium phosphate (Table1) were prepared by conventional melt-quenching technique. Starting reagent ingredients Na₂CO₃, ZnO, CaO, (NH₄) H₂PO₄ and Cu₂O were used for preparation. Appropriate quantities of ingredients are weighed using electric single pan balance of 10^{-3} g sensitivity. The ingredients were then thoroughly mixed by agate mortar. Each composition was taken in an open porcelain crucible and calcined at 340°C for 1hour to release undesired gases; the furnace was then raised to 950°C for 30 minutes. The prepared samples were immediately transferred into preheated stainless steel molds for annealing adjusted at 340°C for 30 minutes. The compositions of the prepared sample are listed in table (1).

Sample	$2\{(NH_4)H_2PO_4\}$	ZnO	CaO	Na ₂ O	Cu ₂ O added
name	Mol (%)	Mol (%)	Mol (%)	Mol (%)	Mol (%)
G_1	42	40	2	14	2
G ₂	42	40	2	12	4
G ₃	42	40	2	10	6
G ₄	42	40	2	8	8
G ₅	42	40	2	6	10

Table (1): Chemical composition of the prepared glass:

XRD diffraction studies were performed at room temperature (RT) using Shimadzu 7000 power diffractometer using CuK_{α} radiation. Glass density measurements were carried out at room temperature using standard Archimedes method with toluene as the immersion fluid (density 0.866gm/cm³). The molar volume (M_v) was calculated from molecular weight M and density ρ . IR absorption spectra of the glasses in the wavenumber range 400-1600cm⁻¹ were recorded at room temperature using FT-IR Perkin Elmer spectrometer. The powdered samples were mixed with potassium bromide (KBr) to obtain thin pellet with thickness of about (1mm). Careful grinding of the samples is of great importance for eliminating error caused by scattering. The optical transmission was recorded at room temperature for the bulk glass samples with the two parallel polished faces using (JENWAY 6405 UV/Vis Spectrophotometer) in the wavelength range (190 - 1100 nm).

3. Results and Discussion:

3.1. Glass Structure:

Prepared free bubble samples are shown in Fig. (1) where the change of colour from blue to tan due to Cu ions is clear. XRD patterns of the prepared glasses in the powder form are presented in Fig. (2). No diffraction peaks are observed indicating the non-crystalline nature of the samples, where a broad hump centered at $2\theta_{-2}20^{\circ}$ - 30° for all the samples, is observed.



Fig. (1): Typical Photographs of ZnNaCaP glass doped with Cu ions



Fig.(2): XRD Patterns for as the prepared at: (a) x= 2mol %Cu₂O, (b) x= 4mol% Cu₂O and x=6mol% Cu₂O.

The dependence of density ρ and molar volume M_v on Cu content is shown in Fig. (3). For ranges x= (2-4%) and x= (8-10%), ρ and M_v show opposite trend. On the other in the range x= (4-8%), both ρ and M_v follow common pattern, where both increase with increasing Cu₂O content. The first case the replacement of light sodium ions by the heavier copper ions is responsible for the increasing density by the copper addition, which is the normal behavior [15-17]. In the second case we are dealing with two competing factors the atomic weight of the additives (copper) and the number of NBO's which responsible for the formation of open structure leading to low density. It seems that in this range (4-8%), the effect of NBO's is more effective than that of increasing density due to the replacement the sodium ions by copper ions [18].



Fig.(3): The variation of density and molar volume.

Figure (4) shows the FTIR spectra in the range between 400-1600cm⁻¹. The spectra contain a number of strong bands beside some shoulders which are characteristic of four main groups of the stretching and bending vibrations of phosphate glass. The broad band confirms the amorphous nature of the studied samples. There is no significant difference in the band positions, i.e., band position is independent on composition.



Fig.(4): Infrared spectra of glasses in the system at: (a) $x = 2 \mod \% Cu_2O$, (b) $x = 4 \mod \% Cu_2O$ and $x = 6 \mod \% Cu_2O$, (d) $x = 8 \mod \%$ and $x = 10 \mod \%$

The vibration modes of the present phosphate network are mainly active in three IR spectral regions (i) in the region1600–820cm⁻¹, (ii) in the region 820–680cm⁻¹ and (iii) in the region 680–400cm⁻¹. The broad absorption band located at 1400-1200cm⁻¹ is attributed to the asymmetric stretching vibration of P=O bond, v_{as} (P=O); this band may also consist of bands due to asymmetrical vibrations of (PO₂)⁻ mode, v_{as} (PO₂)⁻, in metaphosphate units often called Q² units. The Q² units has two NBO's, which are usually assumed to be different since the first terminal oxygen is bounded by P=O, while the other terminal oxygen forms P-O⁻ bond. The weak band at 1140-1160cm⁻¹ is usually attributed as symmetric stretching modes, v_s (PO₂)⁻¹ of metaphosphate chains. The band at 1096-1124cm⁻¹ is attributed to asymmetric stretching modes, v_{as} (PO₃)²⁻, of pyrophosphate groups. The weak band at1030-1076cm⁻¹ is assigned to symmetric stretching mode of (PO₃)²⁻, units. The band at 853-959cm⁻¹ is attributed to the asymmetric vibrations, v_{as} (P-O–P), of bridging oxygen atoms in phosphate

chains. The absorption band at 853-900 cm⁻¹ is attributed to asymmetric stretching vibration of P–O–P groups linked with linear metaphosphate chain[20] while that at 960 cm⁻¹ is assigned to asymmetric stretching of P–O–P groups linked to large metaphosphate rings. The band at 750cm⁻¹ may be attributed to symmetric stretching vibrations, v_s (P–O–P), of bridging oxygen atoms. The broad band around 400- 600cm⁻¹ is most likely due to the bending vibrations of basic structure such as O-P-O and/or O=P-O [7, 9-19]. The band which at > 1400cm⁻¹ may be due to P-OH [7]. The assignment of all observed bands is listed in table (2).

Sample	υ _{as} (/υ _{as} (P=O) PO ₂) ¹⁻	υ _s (P	O ₂) ¹⁻	υ _a (PO	s 3) ²⁻	υ _s (PO ₃)	2-	υ (PO	as 4) ³⁻	υ (P-0	^{as})-P)	υ (P-O	s)-P)	δ(F δ (net	PO ₄) twork)
name	С	Α	С	Α	С	Α	С	А	С	А	С	Α	С	А	С	Α
x=2mol	1196	63.2	1149-	33	1096	61	1047	54	1006	36.1	895-	68	700-	29	604-	85.1
%Cu2O	1204	90.2	1140								853-	16	737	42	566	23.6
	1238	36		34							959	83	773	93	540	28.7
	1271	47.2													527	25.1
	1297	55.8													492	40.2
	1331	67.6													448	68.1
	1396	6.2														
x=4mol	1197	54.5					1034-1063	4.2	977-	56.3	907-	142	707-	61	578	166.5
%Cu2O	1245	46.5						38.5	1008	24	924	6.2	777	94	554	9.5
	1302	68.6													535	6.6
	1298	34													510	34.9
	1388	114													498	30.2
															472	27.6
- 1	1202	0.1	1150		1100		1020 10 5	10.0	007	20.2	010	1.67	510	20	449	36.8
x=6mol	1202	91	1159	3.7	1122	27	1030-1067	10.8	997	39.3	918	165	710-	29	580	128
%Cu2O	1298	76						69.7					113	107	580	65.2
	1336	206													410	235.4
	1196	102	1160	51	1111	37	1045-1076-	13.5	1006	35	918	121	705-	24	596	88.6
x=8mol	1250	108						26.7					772	75	539	40
%Cu2O	1311	17.3													503	24
	1314	199													492	30
															469	17
															436	37
10 1	1201	107			1104	50	1020 1070	10	000	15.0	022	101	704	10	500	
x=10mol	1201	127			1124	52	1030-1069	12	996	15.2	923	101	704-	10	589	66.7
%Cu2O	1307	30.337						26.2					/62	00	540	25.2
	1400							30.2							J14 100	23.2
															400	14.4
															4/5	20.00

Table	(2):	Assignm	ent of	IR	spectra,	where	C is	the	range	componen	it band
	cen	ter (cm ⁻¹)	and A	is th	ne relativ	e area 9	% of	the c	ompon	ent band [2	20-23]:

In general, the shift in the frequency of the band is usually related to the change in the in-chain P–O–P bond strength and angle depending on the nature of the ions linked to phosphate glass structural units [15-17]. Such changes in IR spectra of the studied glasses could be related to the incorporation of copper ions in the phosphate glass network. More precisely, these changes in the IR spectra are due to the formation of short chains of phosphates or decrease in the average phosphate chain length [19, 15-17]. It has already been reported that addition of

cuprous oxide into the glass network no additional bands are observed. However, there is decrease in the area of meta, pyro and orthophosphate groups which suggests presence of Cu₂O that act as a modifier causing a reduction of phosphate groups or more disorder in the glass [18]. In such cases x = (4-8) %, the behavior is different. Since the modifier leads to increasing NBO's, i.e., enhance open structure [15-7]. These results are in consistence with the result of molar volume.

3.2. Optical properties:

Fig. (5) shows the optical transmission spectra at room temperature which were recorded in the wavelength range (190-1100nm). The figure shows single broad transmission band. The behavior of the system reveals a band pass filtering effect. This peak has been assigned due to overlapping of the electronic transition from ${}^{2}A_{1g} \rightarrow {}^{2}B_{1g}$, ${}^{2}B_{2g} \rightarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \rightarrow {}^{2}B_{1g}$ energy terms in the distorted octahedral symmetry of Cu¹⁺ and Cu²⁺ ions in glasses [8]. At x=2%, the band begins with UV spectrum region extends into visible region and ends near infrared spectrum region. This band reveals broad and asymmetric width. The $\lambda_{cut-off}$ is the wavelength at which the percentage transmission is zero. By increasing the concentration of the Cu ions, the $\lambda_{cut-off}$ shifts to higher wavelength and the width of the peak decrease (table 3), i.e., the transmission band is enhanced. The spectra indicate that it tends to shift to lower wave length at x=10 mol%. The absorption coefficient, α , is related to the light is transmitted out of a sample of thickness d, is given by,



Fig.(5): Uv transmission spectra of alkali alkali -earth zinc phosphate glasses doped with different amount of Cu₂O

$$\alpha = \frac{1}{d} Ln \frac{I_0}{I_c} = 2.303 \frac{A}{d}$$
(1)

where I_o and I_t are the intensities of incident and transmitted light, respectively, and A is the absorbance for each sample. Absorption coefficient follows the empirical relation [20].

$$\alpha = B \left[\frac{\left(hv - E_{opt}\right)^2}{hv} \right]$$
(2)

where B is a constant, hv is the incident photon energy and E_{opt} is the optical band gap. The values of E_{opt} for the samples have been calculated by extrapolating the linear region of the curves to meet the hv axis at $(\alpha hv)^{1/2}=0$ as shown in fig. (6) and were presented in Table(3). The band tail associated with valence band and conduction band extend into band gap and show an exponential behavior. The band tails are characterized by parameter E_0 (Urbach energy) which is the width of localized levels in the gap. The values of E_0 can be estimated from the following relation [21]:

$$\alpha (hv) = C + e^{\frac{2}{E_0}}$$
(3)

where C is a constant. The values of E_0 were found as the inverse slope of the ln α versus hu plot as shown in Fig. (7) and are presented in Table(3). From the Fig. (7) and table (3) that it can be seen that the E_{opt} decrease while E_0 increases with increasing the copper content except at x=4%. It is observed that the maximum band tail width and the minimum band gap is observed for x=4%. This allows to assume that sample of x=4% exhibits the highest disorder.



Fig. (6): The variation of $(\alpha h \upsilon)^{1/2}$ with h υ



Fig. (7): The variation of the $(Ln\alpha)$ with hv for all glass samples.

Table	(3):	Optical	absorption	edge	$\lambda_{\text{cut-off}}$,	band	width,	Eopt	and
		Urbach er	nergyE ₀ :						

Х	$\lambda_{\text{cut-off}}(nm)$	W(cm)	E ₀ (ev)	E _g (ev)
2mol%	318	360	0.5435	2.92
4mol%	379	175	1.22	1.167
6mol%	460	110	0.7599	1.33
8mol%	484	95	0.869	1.25
10mol%	460	50	1.142	0.333

Generally, the absorption in the UV region is mainly due to Cu^{1+} , however, the Cu^{2+} ions is responsible for the long wavelength. This is the reason transmission in the visible range spectra. By increasing the copper ions content the width of the peak decrease due to decrease in Cu^{2+} ratio. Since the tail of the transmission band of Cu^{1+} overlap with the edge of the transmission band of Cu^{2+} in the visible region, so the minimum transmission is resultant overlapping. So it is deduced that this minimum point depends on the Cu^{1+} / Cu^{2+} ratio and also is responsible of the colour changes [7]. On the other hand, the peak position is assigned to the middle transition ${}^{2}B_{2g} \rightarrow {}^{2}B_{1g}$ which is directly depending on Cu^{1+} / Cu^{2+} ratio. Also the other two transitions ${}^{2}A_{1g} \rightarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \rightarrow {}^{2}B_{1g}$ (first and third band) are directly depending on Cu^{1+} / Cu^{2+} ratio.

Conclusions:

The glass system [42%P₂O₅- 40%ZnO- 2%CaO- (16-x) %Na₂O- xCu₂O] where x=2, 4, 6, 8 and 10mol% has been prepared by conventional melt quenching technique. The structure of these glasses was confirmed by XRD and infrared spectroscopy. The density and molar volume have been estimated and showed two trends. Optical transmission showed band pass filtering (300-700nm). E_{opt} decrease with increasing the Cu¹⁺ / Cu²⁺ ratio and exhibits opposite trend to E₀.

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