

Application of Cu₂O-doped phosphate glasses for bandpass filter

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ABSTRACT

Phosphate glasses doped with copper ions having general composition 42P₂O₅–39ZnO–(18–x) Na₂O–1CaO–xCu₂O [x=2, 4, 6, 8, 10 mol%] were prepared using a conventional melt-quench technique. Physical and chemical properties of the glasses were investigated using X-ray diffraction technique and UV–visible optical absorption. The density was measured by Archimedes' method, and molar volume (V_M) was calculated. It is found that density and molar volume show opposite trend by increasing Cu₂O content. Absorbance and transmittance at the normal incidence are measured by a spectrophotometer in the spectral range of 190–1100 nm. Analyses of the obtained results were considered in the frame of current theories. Absorption data were used for absorption coefficient, the optical band gap (E_{opt}), the cutoff in UV and IR bands to the bandpass filter, which confirmed the optical properties of this type of filter. E_{opt} values for different glass samples are found to decrease with increasing Cu₂O content.

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1. Introduction

Phosphate glasses find enhanced interest because of their peculiar properties, such as high thermal expansion coefficients, low dispersion, low melting and softening temperatures, high electrical conductivity and optical characteristics [1–3]. Copper-doped phosphate glasses exhibit interesting electrical and optical properties that make them suitable for use as super-ionic conductors, solid state lasers, and can be doped with high level by metal ions and remain amorphous [1]. However, the poor chemical durability of phosphate glass is one of the main disadvantages of using this type of glass, but limit its use in many applications [4,5]. Addition transition metal oxide modifier for phosphate glass has improved the chemical durability [6]. ZnO acts as a good glass modifier, because Zn ion acts as an ionic cross linker between different phosphate anions, inhibiting hydration reaction [7,8]. ZnO shows a different effort on the properties of glasses. For example, Montagne et al. [9] reported that the chemical durability of ternary ZnO–Na₂O–P₂O₅ glasses increased and then decreased, and the density of glass was found to increase with the increase of ZnO [9].

Copper phosphate glasses exhibit an optical absorption band in the visible-near infrared region and fundamental optical absorption edge in the ultraviolet region, i.e. it can be used as bandpass

filter. The Cu²⁺ ion glass exhibits an optical absorption band in the visible region [10]. Phosphate glass doped with copper and its structure were studied by many techniques such as XRD, NMR, XPS, EXAFS, FTIR, Raman spectroscopy, hardness, and electrical conductivity [11–18].

Filters are generally used to lower the overall intensity of the light. These types of filters work by selective absorption and transmittance, and are known as colored glass filters, while other filters work by selective reflection and transmittance, commonly referred to as interference filters [19]. The competition between the interference filters and absorption filters is increasing, but the technology of fabricating the absorption bandpass filters is still very expensive and needs to have more development in chemical composition to reach the optimum practical applications [20].

Study of some physical properties such as density, molar volume, XRD, transmission and absorption was carried out to examine the effect of increasing copper oxide in the expense of sodium oxide on sodium zinc phosphate glass for glass absorption filter applications.

2. Experimental

2.1. Glass preparation

Copper phosphate glasses having the general composition 42P₂O₅–39ZnO–(18–x) Na₂O–1CaO–xCu₂O [x=2, 4, 6, 8, 10 mol%]

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were prepared by the conventional melt quenching technique and shown in Table 1. Analytical grade ingredients of Na_2CO_3 , ZnO , CaO , $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, and Cu_2O were purchased from El-Nasr Pharmaceutical Company, Egypt. These materials were used as starting materials. Corresponding weights of each composite were mixed and ground using agate mortar and then heated in porcelain crucible using a muffle furnace for about 1 h in 330°C in order to release gases. Then the samples were heated at 1100°C for 30 min. The melts were shaken several times to ensure high homogeneity. After quenching the samples were annealed at 330°C for 4 h and then the samples were left to be cooled at room temperature. Finally, the casting quenched and annealed in copper mold with pressing plate to have thin disks for studying the optical properties; thin disk samples were transparent and exhibited green color.

The annealing technique is required because of the internal stress that remained in the glass during quenching.

2.2. Density measurements

Density measurements were carried out at room temperature, using Archimedes' method with toluene as the immersion fluid and applying the following relation [21]:

$$\rho = \rho_L (W_a / W_a - W_L) \quad (1)$$

where ρ_L is the density of toluene, W_a and W_L are the sample weights in air and in toluene, respectively.

2.3. X-ray diffraction analysis

XRD was carried out on glass powders to confirm the amorphous nature of the glasses. Measurements were carried out on a Bruker-D8 Advance Diffractometer (Brüker, UK) in flat plate geometry, using Ni filtered $\text{Cu K}\alpha$ radiation. Data were collected using a Lynx Eye detector at 2θ values from 10° to 90° .

2.4. UV-visible absorption measurements

Ultraviolet and visible optical transmission spectra were immediately measured for perfectly polished glass samples using a recording double beam spectrophotometer (type JASCO Crop., V-570, Rel-00, Japan) covering the wavelength range from 190 to 1100 nm.

3. Results and discussion

3.1. Density and molar volume

The values of density (ρ) and molar volume (V_M) of glass samples have been calculated by Eq. (1) and the molar volume according to this relation: $V_M = M/\rho$ where V_M is the molar volume, M is the glass molecular weight and ρ is the density of the glass, and their values are shown in Table 1. Dependence of density and molar volume with mol% of Cu_2O is shown in Fig. 1. Density is found to increase linearly with increasing Cu_2O content in all investigated range (Fig. 1 and Table 1). This is most likely related to the difference in atomic weights of Cu_2O and Na_2O . Such behavior is generally observed when increasing the content of a modifier oxide in metaphosphate glasses. The molar volume V_M decreases by increasing the Cu_2O content.

3.2. X-ray diffraction analysis

The XRD measurement for glass powders was recorded in the 2θ range of 10° – 90° by using a computer for controlling the

Table 1

Composition of P_2O_5 – ZnO – Na_2O – CaO – Cu_2O , density (ρ) and molar volume (V_M).

Samples	Glass composition (mol%)					ρ (g cm^{-3})	V_M ($\text{cm}^3 \text{mol}^{-1}$)
	P_2O_5	ZnO	Na_2O	CaO	Cu_2O		
S ₁	42	39	16	1	2	3.145	33.28
S ₂	42	39	14	1	4	3.204	33.17
S ₃	42	39	12	1	6	3.279	32.91
S ₄	42	39	10	1	8	3.332	32.87
S ₅	42	39	8	1	10	3.387	32.82

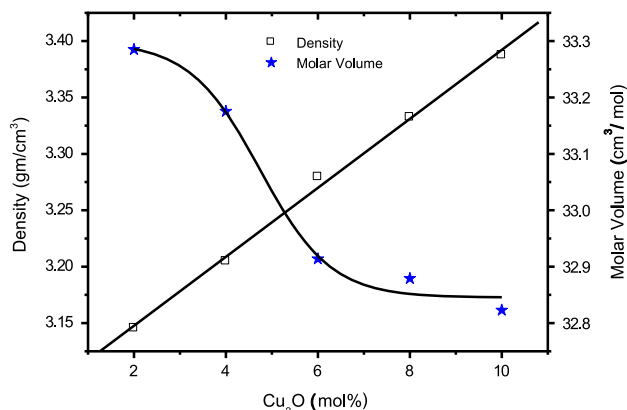


Fig. 1. Density and molar volume of P_2O_5 – ZnO – Na_2O – CaO containing different amounts of Cu_2O .

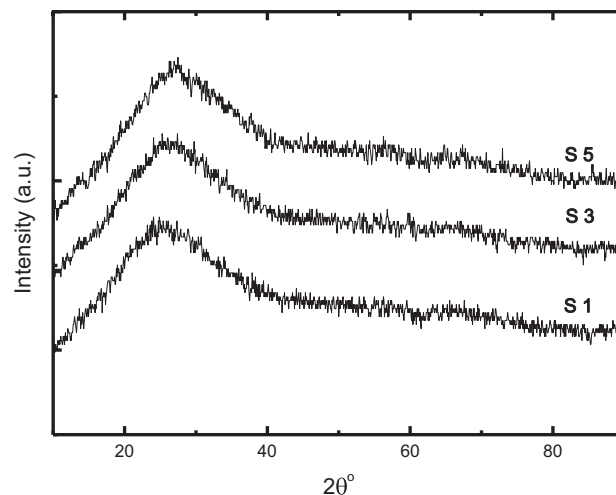


Fig. 2. XRD pattern of the prepared P_2O_5 – ZnO – Na_2O – CaO – Cu_2O .

diffractometer with $\text{Cu K}\alpha$ source. Fig. 2 shows representative XRD patterns of glass powder where no peaks are observed. The obtained data reveal the amorphous nature of the prepared glasses and the presence of random copper phosphate network in the samples.

3.3. UV-visible absorption measurements

3.3.1. Absorption spectra

The absorption spectra of the glass samples are shown in Fig. 3. The spectra reveal an absorption band effect located in the visible region (370 – 750 nm), i.e. it shows that bandpass filter samples of low Cu_2O content exhibit broad non-symmetrical bands. By increasing Cu_2O content, the bands become narrower and more symmetrical.

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