Optical and Ultrasonic Properties of Chromium Oxide in Sodium Zinc Phosphate Glass

Hamdan. A. S. Al-Shamiri[1], A.S. Eid[2]

[1]Department of Physics, Faculty of applied Science, Taiz University, Republic of Yemen

[2]Department of Physics, Faculty of Science, Menoufia University, Shebin El-Koom, Egypt

[1]h_elshamiri@yahoo.com; [2]aseidph@yahoo.com

Abstract-**Sodium zinc Phosphate glasses (NZP) containing different concentrations of chromium oxide have been synthesized by melt quenching technique. Characterization of these glassy materials was carried out by X-ray diffraction, FT-IR spectroscopy. Transmission, absorption and fluorescence as optical properties were also investigated. The optical band gaps (E_o) and energy tail (ΔE) were determined and it was found that, the optical band gap increased with increasing of Cr_2O_3 concentration and vice versa for energy tail. The ultrasonic compression and shear wave velocity measurements were made by pulse-echo technique at a frequency of 5 MHz. The elastic constants of the studied glasses were calculated. The density, molar volume, the ultrasonic wave velocities (longitudinal and shear), the elastic moduli, Poisson's ratio, Debye temperature, mean ultrasonic velocity and the ultrasonic attenuation are found to be sensitive to the glass composition. The compositional dependence of the glass hardness was also examined.**

Keywords-Phosphate Glass; Transition Metals; Optical Properties; Ultrasonic

I. INTRODUCTION

Recent technological applications have generated more interest in the studies of different types of glasses. One of them is pure phosphate (P_2O_5) glass, which due to their hygroscopic nature and volatility was not considered to have industrial and technological applications. But in the recent developments of novel compositions [1-6] of superior physical and chemical properties such as high thermal expansion coefficients [7], low melting and softening temperatures and high ultra-violet and far infrared transmission [8,9], make these glasses potential candidates for many technologically applications, such as sealing materials, medical use [10], and solid state electrolytes [11]. Also because of their unusually high chemical durability and low processing temperature, iron phosphate glass are being considered for vitrifying certain nuclear wastes that are poorly suited for borosilicate glasses [12,13]. Phosphate glasses are also becoming important in optical technology such as in high energy laser application [11], fiber and optical lenses [14, 15]. The relationship between the structure of the host glass and the properties of the doped ions is useful for designing the glasses for different applications. Phosphate glasses containing transition metal oxides (TMO) are of continuing interest because of their applicability in memory switching, electrical threshold, and optical switching devices, etc. [16-18]. The transition metal ions are used as dopants in glasses mainly for two reasons: firstly, their well defined and sharp energy levels may serve as structural probes for the environment of the dopant. And secondly, the modifications of the energy level structure of the transition metal ions caused by the glassy environment may lead to interesting applications, such as new lasers and luminescence materials. The technological applications of the phosphate glasses are clear, so a better understanding of the optical and mechanical properties of these glasses could lead to further applications or improved glass composition. However, the aim of the present study was to investigate the effect of Cr_2O_3 concentration on optical properties and the glass forming characteristics of sodium zinc phosphate (NZP) glasses. Glasses of the general composition 30 Na_2O + 20 Zn O + 50 P_2O_5, with different concentration of Cr_2O_3, were prepared by conventional melting and investigated by X-ray diffraction analysis (XRD), FT-IR spectroscopy, UV-visible absorption and fluorescence spectroscopy, and pulse echo technique to elucidate the structure of the glasses.

II. EPERIMENTAL PROCEDURES

A. Glass Preparation

The glass specimens were prepared from analar grades of sodium oxide, Na_2O, zinc oxide, ZnO, phosphorus pent oxide, P_2O_5, and chromium oxide, Cr_2O_3, in 99.99 % purity. The appropriate quantities based on this formula 30 Na_2O + 20 Zn O + 50 P_2O_5 + x wt % Cr_2O_3 where x = 0, 0.002, 0.004, 0.006, 0.008 , 0.04 and 0.06 wt %, were mixed together into an alumina crucible and inserted into an electric furnace held at 300 oc for one hour. This allows the P_2O_5 to decompose and react with other batch constituents before melting. After this treatment, each mixture was transferred to another electric furnace open to the atmosphere with its temperature pre-adjusted at from 1030 to 1050 ^{o}C. The molten was occasionally stirred with an alumina rod to ensure homogeneity and retained in the furnace for half one our. Then the melt was poured onto two mild steel split mould heated to 300 oC to form glass rods of 0.5 cm long and 1.6 cm diameter. After casting each glass was immediately transferred to an electric furnace held at 300 ^{o}C for one hour. Then the furnace was switched off and the specimens were allowed to cool to room temperature, at as initial cooling rate of ~ 3°c per minute. Finally, the glass samples were cut and polished. The glasses show the typical green colour of the Cr_2O_3.

B. X-ray Diffraction Analysis

XRD was obtained from X-ray Diffractometer (Bruker AXS, Model: D8 Advance, UK) using CuKα as a radiation source at a scanning rate of 2□ per min. The XRD analysis was used to confirm the amorphous nature of the glasses.

C. Optical Absorption and Emission Measurements

The optical absorption and fluorescence spectra were recorded at room temperature using a UV–visible spectrophotometer (Hitachi, U-1800) working at 190–1100 nm. Steady state emission spectra were measured with Perkin-Elmer Spectrophotometer and Ls-50B luminescence

spectrometer using a special front to face sample attachment. The absorption coefficient, α (ν), was calculated for each sample at different photon energies by the relation [19]:

$$\alpha\ (\nu) = (1/d)\ ln\ (I_0\ /\ I_t) \qquad (1)$$

Where d is the thickness of the samples, I_0 and I_t are the intensities of incident and transmitted radiations, respectively.

D. Infrared Measurements

The IR absorption spectra of the studied glasses were measured for each glass sample over the range, 4000 to 400 cm^{-1}. A JASCO 460 FTIR (made in Japan) infrared spectrometer was used in conjunction with the potassium bromide, KBr, disc technique. Samples of glass weighing 0.004 g were mixed and ground in a clean mortar to a fine powder with 0.200 g of KBr. After which, the mixture was pressed at 15 tons for three minutes under vacuum, yielding transparent discs suitable for mounting in the spectrometer.

E. Density Measurements

The Archimedes method was employed to determine the glass density, ρ, using toluene ($\rho t = 0.653$ gm/cm^3 at 25 °C) as an immersion liquid according to the following equation:

$$\rho = \rho_t\ (W_a - W_{a1})/\ [(W_a - W_t) + (W_{t1} - W_{a1})] \qquad (2)$$

Where, Wa is the weight of the glass in air, Wt is the weight of the glass in toluene and Wa1, Wt1 are weights of suspended thread in air and toluene, respectively. Repeated density measurements were agreed within ± 0.01 %. The molar volume, V_m, of each glass was calculated by using this equation: $V_m = M / \rho$, where, M is the molecular weight of glass components.

F. Ultrasonic Measurements

In this work, a version of the conventional pulse echo technique using an ultrasonic flaw detector (Krautkramer USM2) was employed. In this apparatus, one transducer is used as transmitter and receiver at the same time. Quartz crystals X and Y-cuts, of same operating frequency (5MHz) were used to produce longitudinal and shear ultrasonic waves, respectively. These crystals were bonded to the glass specimens by silicon grease as an acoustic coupling. Tested glasses were prepared in disc form with highly polished and parallel faces, 2.5 mm thick and 1.5 cm diameter. Both of the specimen and the crystal were put together in a sample holder connected to the ultrasonic flaw detector. This technique is characterized by its exponentially and equal spaced pattern of echoes which enables us to determine the ultrasonic attenuation of the waves propagated in the glass according to this equation [20]:

$$\varphi = \{-20/\ 2(m-n)\ L\}\ log\ (A_m/A_n) \qquad (3)$$

Where, Am and An are the maximum amplitudes (voltages) of the mth and nth pulse echoes respectively, L is the specimen thickness. Calculated values of φ for prepared glasses were accurate to ± 0.1 % dB/cm. Also, from the average transit time spacingΔt between successive echoes on the screen of the CRT of the detector and the length of the specimen, both of the longitudinal and shear wave velocities, V_l and V_s are determined with precision of about ± 0.03 % m/s. Hence, values of elastic moduli and Poisson ratio are calculated according to the well-known equations:

$$\text{Longitudinal modulus,}\quad L = \rho\ V_l^2 \qquad (4)$$

$$\text{Shear modulus,}\quad G = \rho\ V_s^2 \qquad (5)$$

$$\text{Bulk modulus,}\quad K = L - (4/3)\ G \qquad (6)$$

$$\text{Young's modulus,}\quad E = G\ (3L - 4G)\ /\ (L - G) \qquad (7)$$

$$\text{Poisson's ratio,}\quad \sigma = (L - 2G)\ /\ 2(L - G) \qquad (8)$$

Where, ρ is the glass density.

The hardness of the glass could also be calculated by using the following equation [21, 22]:

$$H_{cal} = (1 - 2\sigma)\ E\ /\ 6(1 + \sigma) \qquad (9)$$

And the Debye temperature which represents the temperature, at which all modes of vibrations in a solid specimen are excited, is calculated according to [23, 24]:

$$\Theta_D = (h/k)\ [9N\ /\ 4\pi\ V]\ V_m \qquad (10)$$

Where Vm is the mean ultrasonic velocity given by:

$$3/V_m^3 = (l\ /V_l^3)\ +\ (2\ /V_s^3) \qquad (11)$$

Where, h is the Planck's constant, k is the Boltzmann constant and (N/V) is the number of vibrating atoms per unit volume (= p N_A, p is number of atoms in the chemical formula, and N_A Avogadro's number).

G. Microhardness Measurements

Vicker's microhardness, H, of prepared glasses was measured at room temperature by using an Microhardness tester (HMV -2, Ver. 1.28, Shimadzu, Japan). The sample was polished very good with two parallel faces and then put in the tester at force, F, equal 4.903 N for 30 second for 7 times by using the equation [25]:

$$H = \frac{18.19F}{D^2} \qquad (12)$$

Where, D is the diameter of the indentation.

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of all the sodium zinc phosphate glasses doped with different concentration of Cr_2O_3 show broad peaks around 20-30° and 40-50° (2Θ values), which confirm the amorphous nature of all the synthesized glassy samples.

A. Density and Molar volume

Density is one of the effective tools to explore the degree of structural compactness. The density and molar volume of the glass network depend upon many factors such as structure, coordination number, cross-link density, and dimensionality of interstitial spaces [26].

Experimental values of density and molar volume are tabulated in Table I. The density, ρ, is increased with relatively high rate in the compositional range from 0 to 0.008 wt % of Cr_2O_3 (ρ increased from 2.7402 to 2.8608 g/cm^3). As the concentration of Cr_2O_3, raised beyond 0.008 Wt %, the increasing rate of the density is slow (ρ increased from 2.8608 to 2.9107 g/cm^3). Also the decreases of molar volume Vm with Cr_2O_3 content varies with high rate up to 0.008 wt % (Vm decreases from 38.6243 to 36.9966 cm^3), behind 0.008 wt %, the V_m varies with slow rate (V_m decreases from 36.9966 to 36.368 cm^3) as shown in Fig 1.

TABLE I   DENSITY (P), MOLAR VOLUME (V_M), ABSORPTION EDGE (ΛE), OPTICAL BAND GAP (E_{OPT}), AND URBACH ENERGY (ΔE), LONGITUDINAL VELOCITY (V_L), SHEAR VELOCITY (V_S), OF (30 Na_2O + 20 ZnO + 50 P_2O_5 + X W_T % Cr_2O_3) GLASSES.

| Sampl.	ρ	V_m	λ_{edg}	E_{opt}	ΔE	V_L	V_s
Wt %	gm/cm^3	cm^3	(nm)	(ev)	(ev)	m/s	m/s
0	2.740174	38.62429	274	3.0259	0.5212	2672	1636
0.002	2.744844	38.55881	270	3.0411	0.5149	2835	1736
0.004	2.796157	37.85144	266	3.0512	0.5071	2926	1793
0.006	2.837494	37.30024	264	3.0840	0.5002	3065	1879
0.008	2.860799	36.9966	262	3.1172	0.4971	3205	1966
0.04	2.884746	36.69305	258	3.1994	0.4865	3520	2160
0.06	2.910709	36.36797	254	3.2128	0.4739	3672	2254
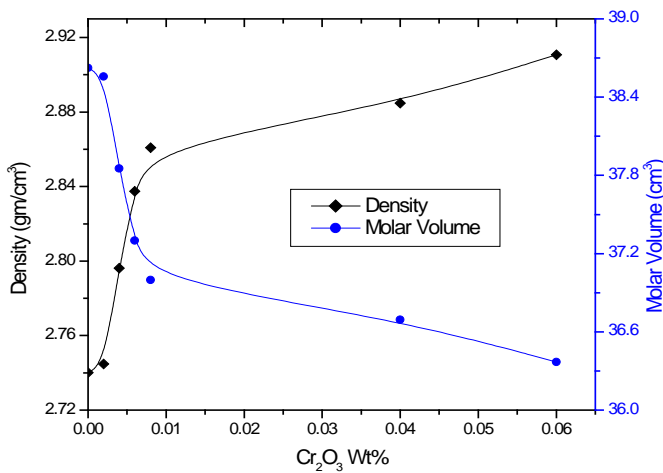
Fig. 1 Variation of density and molar volume with Cr_2O_3 wt% for sodium zinc phosphate (NZP) glass system

The density of the glasses depends on the compactness of the structural units [27]. The increase in density is attributed to changes occurred in the volume concentration of PO_4 units, and modification of the geometrical configurations of the glass network leads to changes in the coordination and variation of the interstitial holes. Also molar volume V_m depends on both the rates of change of density and molecular weight. However, when the Cr_2O_3 concentration is increased, the increasing rate of density is greater than that of molecular weight. The results obtained from studies of density and molar volume V_m indicate that the Chromium oxide lower the concentration (0.008 wt %) enters the glass network as a modifier by occupying the interstitial space in the network and generating the NBO's to the structure. As the concentration of Cr_2O_3, raised beyond 0.008 Wt % the chromium ions seem to exist in Cr^{6+} state (evidenced from optical absorption spectra), participate in the glass network forming with CrO_4^{2-} structural units.

B. Optical Transmission and Absorption

The transmission spectrum of the un-doped sodium zinc phosphate (NZP) glass in the UV-VIS- NIR range is presented in Fig 2. As observed, the un-doped sodium zinc phosphate (NZP) glass exhibits a relative high optical transmission equal to (86%) in the NIR and most visible range and decreased fast

to zero at nearly 274 nm. The excellent transparency in the infrared (IR) and visible regions make this glass have a potential applications as IR domes, optical filters, modulators, memories and laser windows. Further, this glass is considered as very good materials for hosting lasing ions like chromium.
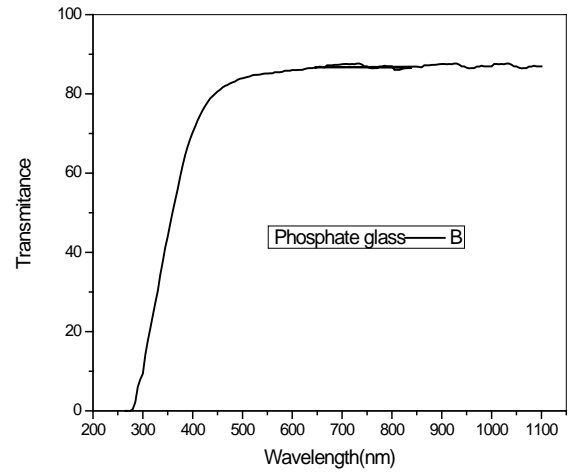

Fig. 2 The transmission spectrum of the pure sodium zinc phosphate (NZP) glass

Absorption spectra of Cr_2O_3 doped sodium zinc phosphate (NZP) glasses are shown in Fig. 3. The spectrum of each glass has exhibited absorption bands at 453 and 641 nm identified due to the conventional transitions of Cr^{3+} ions viz., $^4A_2$ - $^4T_1(F)$ and $^4A_2$ - $^4T_2$, respectively. The intensity of these two bands increases with Cr_2O_3 concentration. As the concentration of Cr_2O_3, increase beyond 0.008 Wt % a new band predicted due to Cr (VI) ions is observed at 370 nm [28] as shown in the inset in Fig. 3. The Cr (VI) ions exist in the form of $Cr^{6+}O_4^{2-}$ centers in the frame of CrO_4^{2-} groups [29]. Additionally two significant kinks at 671 and 712 nm have appeared on 641 nm band in the spectra of the glasses. The dips observed in the $^4A_2$-$^4T_2$ absorption band seem to correspond to Fano anti-resonance mechanism between the $^4A_2$-$^4T_2$ broad bands and spin forbidden transitions $^4A_2$-^2E and $^4A_2$-$^2T_1$ which may induce negative contribution to $^4A_2$-$^4T_2$ band [30]. The optical absorption edges are not sharply defined in glass samples under study, in accordance with their amorphous nature [31]. The pure (NZP) glass has exhibited absorption edge at 274 nm. With the increase in the concentration of Cr_2O_3, the edge is observed to shift gradually towards shorter wavelength. The gradual shifting of absorption edge with increase in the concentration of Cr_2O_3 towards lower wavelengths also indicates an increasing concentration of Cr^{6+} ions that takes part in the network forming positions with CrO_4^{-2} structural units. Lower the concentration of the Cr^{3+} ions that acts as modifiers, which lower the concentration of non-beridging ions (NBO's) in the glass matrix. This leads to a decrease in the degree of localization of the electrons, there by decreasing the donor centers in the glass matrix. The presence of low concentration of the donor centers raises the optical band gap and shifts the absorption edge towards lower wavelength side . From the observed absorption edges, we have evaluated the optical band gap (E_{opt}) of these glasses, from the linear regions of the plots between $(\alpha h v)^{1/2}$ and (hv) as shown in the Fig. 4. The values of optical band gap (E_{opt}) obtained from these plots for (NZP) glasses with different concentration of Cr_2O_3 are

presented in Table 1. The results show that the optical band gap values are increasing with an increase of Cr_2O_3 content. It is pointed out that the optical band gap [32] slightly increases with an increase in Cr_2O_3 and results in the increase in bonding defect and non-beridging oxygen. The increase in E_{opt} on the increase in Cr_2O_3 content is due to the structural changes. This leads to an increase in the degree of electrons localization thereby the increase of donor centers in the glass matrix.
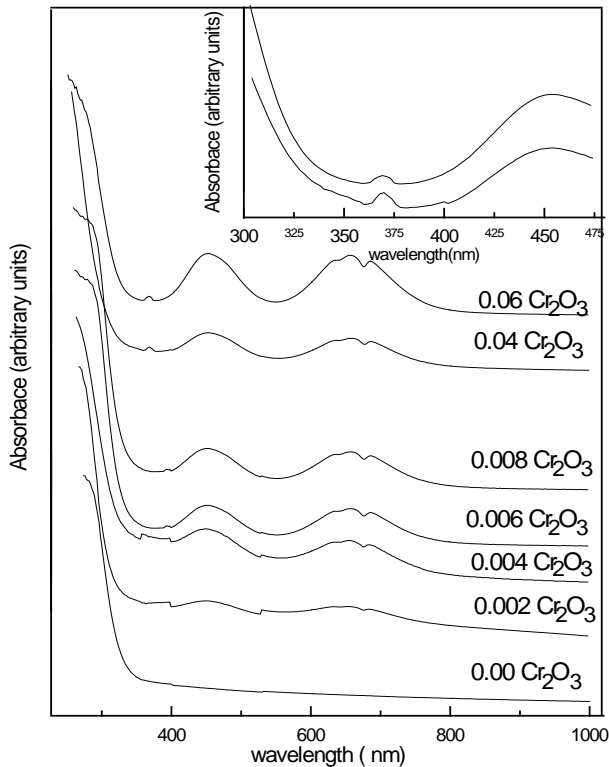

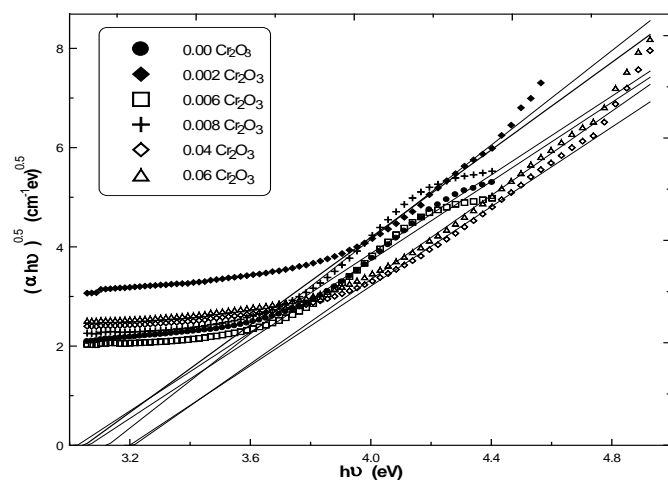Fig. 3 Optical absorption spectra of sodium zinc phosphate (NZP) glass doped with different concentration of Cr_2O_3

Fig. 4 Plot of $(\alpha h\upsilon)^{1/2}$ against photon energy (hυ) for optical band gap (E_{opt}) measurement of (NZP) glass with different concentration of Cr_2O_3

The values of energy tail (Urbach energy) ΔE were calculated from the following equation α (ω) = B exp ($\hbar\omega/\Delta E$). Where, B is a constant, ΔE is known as energy tail or Urbach Energy. The values of energy tail ΔE for 30 Na_2O-20 ZnO- 50 P_2O_5 glasses doped with different concentration of Cr_2O_3 were evaluated and tabulated in Table . M ott and D avies [33] reported that the values of ΔE for a range of amorphous

semiconductors are very close together in value and the range is between 0.05 eV and 0.07 eV. For ΔE value of Na_2O-TeO_2 glasses is reported by Vijaya Prakash et.al.[34] to lie between 0.09 eV and 0.26 eV and in the case of V_2O_5-P_2O_5-TeO_2 glasses Hogarth [35] reported the value of ΔE varies between 0.31 eV to 0.41eV.In the present work, the exponential behavior is observed and the value of ΔE varies between 0.47 eV and 0.52 eV. For this glass system, the exponential dependence of absorption coefficient α (ω) on photon energy ($\hbar\omega$) suggests that these materials obey the Urbach rule. An addition of Cr_2O_3 to the glass system shows increasing in optical band gap and reduction Urbach tails with the densification of the glass network.

C. Fluorescence Spectra

The fluorescence spectra for Cr_2O_3 doped sodium zinc phosphate (NZP) glasses are shown in Fig. 5. The fluorescence spectrum of each glass has exhibited emission bands at 730, 684 and 560 nm identified due to the conventional transitions of Cr^{3+} ions. It has been previously reported that the emission properties of Cr^{3+} are strongly dependent on the nature of its local environment [36–40]. The well-known Tanabe–Sugano energy level diagram for Cr^{3+} ions, which belong to the d^3 configuration [41], shows a crossing point between the highly environment sensitive $^4T_2$ level and the low environment sensitive ^2E level. Since the line width of the bands is directly related with the strength of the electron–lattice coupling between the Cr^{3+} ion and its surroundings, the sites emitting from the $^4T_2$ level, called low-field sites, are characterized by a broad band centered in the near infrared due to a strong electron–lattice coupling. In the same way, the sites emitting from the ^2E level, called high field sites, are characterized by a narrow band in the upper limit of the visible range (around 641 nm) and a weak electron–lattice coupling.
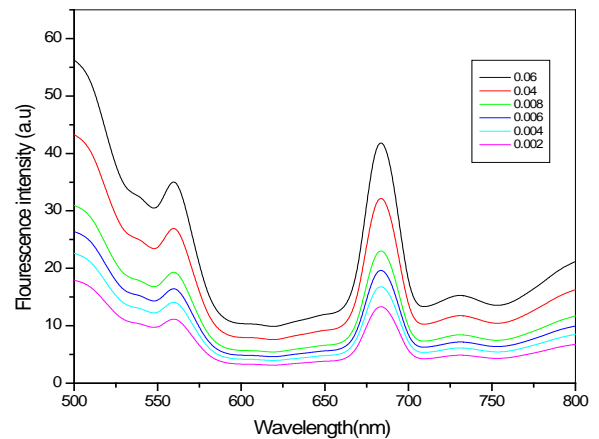

Fig. 5 Fluorescence spectra of sodium zinc phosphate (NZP) glass doped with different concentration of Cr_2O_3

In most of the Cr^{3+}-doped glasses [12, 13, 42 - 44] and in some crystalline structures [45, 46] emission is dominated by low-field sites. This fact has attracted much attention in the development of laser gain media, because of the possibility of a wide tuning range for laser action. However, in glassy matrices, the presence of low-field sites with different absorption and emission spectra gives rise to in homogeneously broadened bands resulting in poor quantum efficiencies.

D. Infrared Spectra

The study of the structure of glasses is very important for the investigation of their properties. IR-transmitting glasses can be highly functional material in terms of the field structures. Fig. 6 shows the plots of the infrared transmission spectra for the vitreous (30 Na_2O + 20 ZnO + 50 P_2O_5+ x Cr_2O_3 glass system in the spectral range 4000 to 400 cm^{-1}).
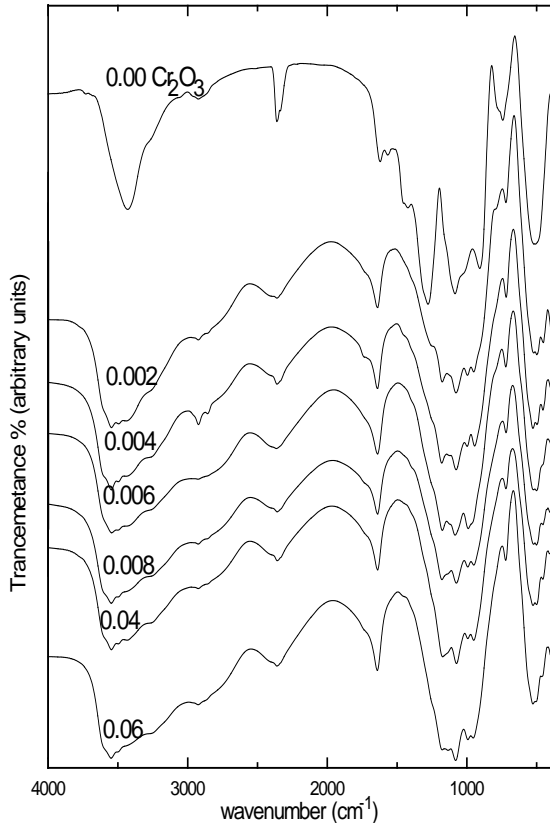

Fig. 6 Infrared spectra of sodium zinc phosphate (SZP) glass un doped and doped with different concentrations of Cr_2O_3

The positions of the absorption bands of the glass samples are listed in Table Ⅱ, with the specification of vibrational modes of broad, strong and weak absorption bands in the investigated range of wave numbers 4000 – 400 cm^{-1}, indicates an amorphous nature of the present glasses. The main absorption bands of the pure sodium zinc phosphate (NZP) glass occur around the wave number 519, 740, 906, 1088 and 1285 cm^{-1} have been assigned to the P-O-P harmonic bending, the P-O-P anti-symmetric, the P-O-P symmetric, the PO_4^{3-} υ_3-normal tetrahedral ion and P=O stretching symmetric vibrational bonds, respectively [47,48]. Also absorption bands found in 1625, 2360, 2420, 3045 and 3436 cm^{-1} are attributed to the water absorbed by the glass samples during the preparation of pellets. After adding different concentration of Cr_2O_3 to the sodium zinc phosphate (NZP) glass, it is clear that in general the mid-band position for each band shifts to higher wave numbers with increasing the wt % of Cr_2O_3 content, the intensity of bands due to P=O, PO_4^{3-}, P–O–P and O=P-O are observed to decrease for further increase of Cr_2O_3 content; this may be attributed to replacing phosphorus ion by chromium ion which confirms the chromium ions enter the glass network, a new peak appear at 455 cm^{-1} attributed to Cr-O, and a peak intensity at 1285 cm^{-1} for (P=O) decreased with increased the Cr_2O_3 concentration until reach (0.006 wt%) ,after that the peak absorption band disappear completely. This result suggests that in this concentration range chromium ions mostly exist in tri-valence state, act as modifiers and disrupt the glass network.

However, when the concentration Cr_2O_3 is raised beyond 0.006 mol %, the chromium ions seem to exist in Cr^{6+} state, participate in the glass network forming with CrO_4^{2-} structural units. As we mentioned before in absorption section, the Cr ions enter the glass network interstitially, as a network modifier; and we know that when modifier cations are added to phosphate glasses depolymerization takes place through the breaking of P-O-P linkages and formation of ionic cross bonding between the phosphate chains.

E. Ultrasonic Velocities and Elastic Moduli

Elastic properties are suitable for describing the glass structure as a function of composition [49]. Elastic properties of phosphate glasses through ultrasound velocity measurements are one of the important techniques to elucidate the structure of glasses. The ultrasonic wave velocities measured in this work are found to be sensitive to the Cr_2O_3 concentration, as shown in Fig. 7. It is observed that both of the ultrasonic wave velocities V_L and V_s are rapidly increased from 0 to 0.008 wt% Cr_2O_3 i.e. V_L increased rapidly from 2672 to 3205 m/s and V_S increased from 1636 to 1966 m/s. As the concentration of Cr_2O_3, raised beyond 0.008 Wt % the ultrasonic wave velocities V_L and V_S are slowly increased from 3205 to 3672 m/s and from 1966 to 2254 m/s respectively.
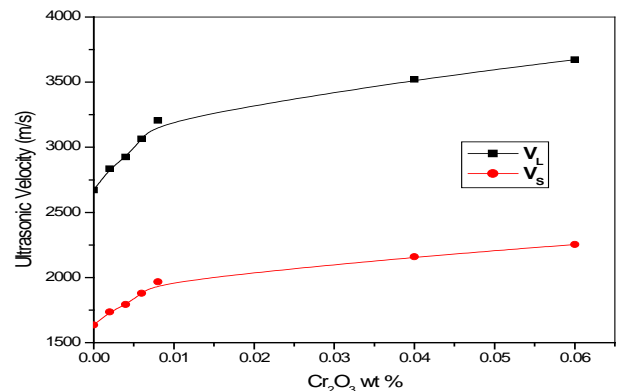

Fig. 7 Variations of ultrasonic wave velocities, V_l (m/s) and Vs (m/s) of (NZP) glasses with wt % of Cr_2O_3 content

In general, the increase of ultrasonic wave velocity is related to the increase in connectivity of the glass network. This increase in ultrasonic wave velocities can be explained by the decrease in molar volume (i.e. the decrease in the inter-atomic spacing) which means that the Cr^{3+} ions with octahedral coordination are involved in the glass network as modifiers by occupying the interstitial positions which cause the increase in the average number of the network bonds per unit volume. Therefore, it can be suggested that the Cr^{3+} ion modification lead to an increase in the network connectivity of the glass under study. Rajendran et al. have investigated the mechanical properties of P_2O_5-Na_2O-CaO-TiO_2 glasses [20]. The authors reported that the transition metal ions enter the glass network in a position which create a cross-linking between the phosphate tetrahedra (TM- O- P instead of P-O-P), and consequently improve the stability and mechanical properties of the glass [20].

The elastic moduli, viz longitudinal (L), shear (G), bulk (K) and Young's modulus (E), have the same behavior of change as the ultrasonic wave velocities (Fig. 8) i.e., they are all rapidly increased (L from 19.56 to 39.26 GPa, G from 7.33 to 14.79 GPa , K from 9.78 to 19.53 GPa and E from 17.60 to 35.42 GPa) with change of increasing rate at 0.008 wt% Cr_2O_3 which increase slowly behind 0.008 wt% Cr_2O_3 in the glass matrix.
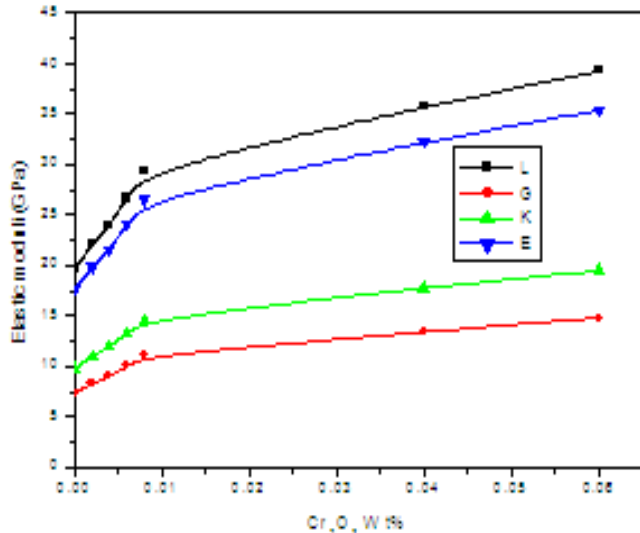

Fig. 8 Variation of elastic moduli of (NZP) glasses with the wt % of Cr_2O_3 content

Table III gives the values of Poisson's ratio σ. They have decreased from 0.2002 to 0.1976 with changing the concentration of Cr_2O_3 ions as in Fig. 9. This decrease in

Poisson's ratio can be explained in terms of ionic bonds that are formed in the glass network [50]. In addition, Bridge and Higazy [51] have suggested a close correlation between Poisson's ratio and cross-link density which is defined as the number of bridging bonds per cation. They reported that the cross-link density of two, one, and zero are related to the values of Poisson's ratio of 0.15, 0.39, and 0.4, respectively.

The Debye temperature (Θ_D) is an important parameter of solids, which represents the temperature at which nearly all the vibrational modes are excited. Calculated values of the mean ultrasonic velocity V_m, Debye temperature Θ_D, of the glass under study are collected in Table 3. It can be observed that the Debye temperature increased from 193.9 K to 272.5 K with change of increasing rate at 0.008 wt% Cr_2O_3. The increase in the mean ultrasonic velocity from 1806.2 to 2487.7 m/s and consequently the increase in the Debye temperature as shown in Fig. 10 is mainly due to the increase of the number of bonds per unit volume as a direct effect of insertion of Cr^{3+} ions into the glass network structure, which implies an increase in the rigidity of the glass network.

This resulted increase in rigidity of these investigated glasses has in turn a great effect on the glass micro-hardness (H) and the ultrasonic attenuation (φ) in the manner that the hard ness (H) is increased, while the ultrasonic attenuation (φ) is decreased as shown in Fig. 9 These increases of H and ecrease decrease of φ show the observable change in the variation rates at 0.008 wt % Cr_2O_3.

Now the correlation between the results obtained in the present work from optical and ultrasonic measurements on the investigated glassy system 30 Na_2O + 20 Zn O + 50 P_2O_5 + x wt % Cr_2O_3 can be approached as follows:

TABLE II FT-IR PEAK ABSORPTION BANDS ASSIGNMENTS OF (NZP) GLASSES; PURE AND DOPED WITH DIFFERENT CONCENTRATION OF $Cr_2\,O_3$

S	Cro	P-O	P-O-P	P-O-P	PO_4^{3-}	P-O⁻	P=O	P-O-H	PO_4^{3-}	PO_4^{3-}	P-O-H
Wt %		bend	Symmet	asymmt	symm			bend	$2v_3$ Te	v_4 Tetra	stretch
0	0	519	740	906	1000	1088	1285	1623	2364	2925	3438
0.002	455	524	728	951	1001	1078	1172	1644	2361	2927	3551
0.004	455	531	721	951	1001	1078	1177	1644	2361	2935	3551
0.006	455	524	728	956	999	1083	1181	1644	2364	2925	3551
0.008	457	536	726	951	1004	1081	1181	1642	2361	2923	3556
0.04	459	527	728	963	997	1078	0	1649	2361	2930	3551
0.06	464	522	721	963	997	1088	1186	1647	2364	2930	3546

TABLE III VARIATION OF LONGITUDINAL MODULUS L, SHEAR MODULUS G, BULK MODULUS K, YOUNG'S MODULUS E, HARDNESS H, POISSON'S RATIO σ, ULTRASONIC ATTENUATION φ, RATIO E/G, DEBYE TEMPERATURES Θ_D, AND MEAN ULTRASONIC VELOCITY V_m OF (30 Na_2O + 20 ZnO + 50 P_2O_5 + X Wt % Cr_2O_3) GLASSES

Samp.	L	G	k	E	H	σ	φ	E/G	Θ_D	Vm
Wt %	GPa	GPa	GPa	G Pa	GPa		m/s		K	m/s
0	19.5637	7.334065	9.784949	17.60398	1.46607	0.200152	6.9264	2.400304	193.9032	1806.145
0.002	22.06093	8.273594	11.02947	19.85591	1.654957	0.199957	6.4285	2.399914	205.8858	1916.675
0.004	23.93923	8.989222	11.9536	21.56258	1.801696	0.199357	6.0286	2.398715	213.9296	1979.304
0.006	26.65606	10.01817	13.29849	24.02227	2.010748	0.198935	5.6867	2.39787	225.2794	2074.146
0.008	29.3862	11.05743	14.64295	26.50154	2.223588	0.198358	5.2275	2.396717	236.3386	2170.048
0.04	35.74316	13.45907	17.79773	32.24825	2.709656	0.198012	5.0942	2.396023	260.3643	2384.094
0.06	39.24678	14.7879	19.52958	35.4229	2.980268	0.197699	4.9124	2.395397	272.493	2487.763

The atomic ring size of the network, the coordination number, the number of bridging bonds (connectivity) and the

force constant of bonds determine the strengthening and weakening of the glass matrix. An increase in the

compactness of the glass structure, (i. e. decreasing the atomic ring size which decreased the molar volume and increased the density of the glass). An increase in connectivity is occurred which is quantitatively confirmed by increasing the value of the cross-linking density. This increase in connectivity and vanishing of P=O absorption band with establishment of new bonds of large force constants i.e. (P-O-M) hence, the increase in the glass rigidity (i.e hardness) which are the reasons, behind the observed increase in ultrasonic wave velocities (V_1 and V_s),elastic moduli (L, G, K and E), the Debye temperature (Θ_D) and optical energy gap Eopt as well as the decrease in the ultrasonic attenuation (φ), Poisson's ratio (σ) and width of the band tail (ΔE).
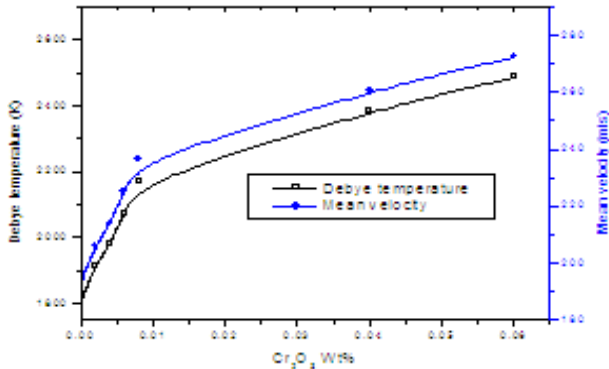

Fig. 9 Variations of Poisson's ratio σ and E/G ratio of (NZP) glasses with wt % of Cr_2O_3 content
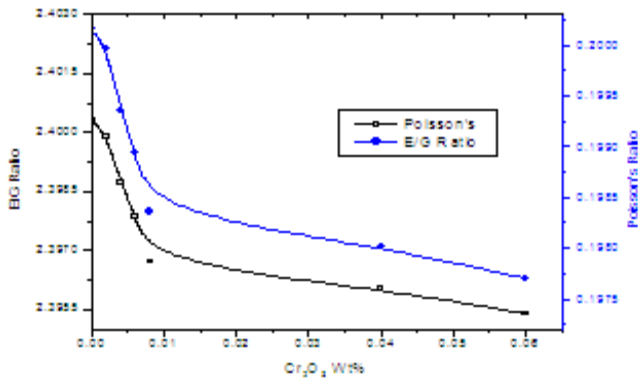

Fig. 10 Variations of Debye temperature and Mean velocity (m/s) of (NZP) glasses with wt % of Cr_2O_3 content
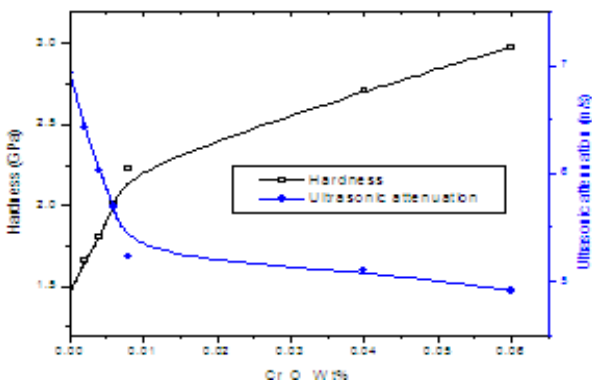

Fig. 11 Variations of Hardness (GPa) and Ultrasonic attenuation (m/s) of (NZP) glasses with wt % of Cr_2O_3 content

IV. CONCLUSION

The sodium zinc phosphate (NZP) glasses were prepared at various doping concentration of Cr_2O_3 and characterized for their physical, optical, and ultrasonic properties. The (NZP) glasses are particularly attractive hosts because they can accommodate large concentrations of active ions Cr^{3+} without losing the useful properties. Chromium ion is a paramagnetic transition metal ion, when dissolved in glass matrix in very small quantities makes the glasses coloured and has a strong influence over the optical and mechanical properties of the glasses. The (NZP) glass density increase with an increase in concentration of Cr_2O_3. The decrease in molar volume with Cr_2O_3 content indicates the extension of glass network due to increase in the number of NBOs. The optical absorption and FT-IR studies indicate that chromium ions mostly exist in tri-valence state Cr^{3+}, in addition to Cr^{6+} states especially when the content of Cr_2O_3 is greater than 0.008 wt%. The value of optical band gap is found to increase with the increase in concentration of Cr_2O_3. The excellent transparency in the infrared (IR) and visible regions, make this glass have a potential applications as IR domes, optical filters, modulators, memories and laser windows. Further, this glass is considered as very good materials for hosting lasing ions like chromium. The ultrasonic wave velocities (longitudinal and shear), the elastic moduli, Poisson's ratio, Debye temperature, mean ultrasonic velocity and the ultrasonic attenuation are found to be sensitive to the glass composition. Finaly from all of these results the authors expect that probability use this type of glass doped with appropriate concentration of Cr_2O_3 as Acsto- optical Q-switching in laser devices

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Hamdan Ali Sultan Al-shamiri born in 06/9/1972 in Taiz Yemen Republic. Scientific qualifications as the following: A warded B.Sc. degree in.1995 from physics department faculty of applied science- Taiz university- Yemen Republic., Diploma in laser physics in 1999 from National institute of laser- enhanced science- Cairo university- Egypt., M. Sc degree in (16/3/2003) from laser system department-National institute of laser enhanced science- Cairo university- Egypt., also Ph.D degree in (18/3/2007) from laser system department- National institute of laser enhanced science- Cairo university- Egypt. He is now assistant professor for laser physics and spectroscopy in physics department–faculty of applied science, and head of physics department in faculty of education–Taiz University. He has more experience in preparation of host materials such as polymer, sol gel glass and hybrid materials for different laser dyes, transition metals and rear earth, and has interested in building and design most laser systems. He has number of research published in worled scientific journals.