

Study of the optical properties of Li₂O modified P₂O₅-Na₂O glasses

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Abstract

Optical characteristics of the prepared glasses of composition 55 P₂O₅ – (45-x) Na₂O – x Li₂O were (0 ≤ x ≤ 35 mol%) have been investigated by X-Ray diffraction (XRD), differential thermal analysis (DTA), density (ρ), molar volume (V_m), optical packing density (OPD), UV spectroscopy and Fourier transform infrared (FTIR). The FTIR studies revealed the vibrational modes of prepared glass samples. Absorbance of investigated glasses was measured and used to estimate their optical absorption coefficient and optical energy gap. The optical studies revealed that the indirect optical band gap (E_{opt}) increases from 3.2-3.5 eV and the Urbach energy decreases from 1.133-0.838 eV with increase of Li₂O content from zero up to 35 mol% Li₂O.

Introduction

The synthesis and physical properties of phosphate glasses have a great potential because of its important technological applications. Phosphate glasses have unique and better physical properties than other glasses such as hardness, transparency at room temperature, low glass transition temperature, excellent corrosion resistance, low melting and softening temperature and high thermal expansion [Yahia H. Elbashar et al. (2016), R.K. Brow et al. (2000), Samir Y. Marzouk et al. (2009), A. Bhide et al. (2007), I. Abrahams et al. (2000)]. Among oxide glasses, lithium and sodium phosphate glass and glass ceramics are used as solid electrolytes for battery applications [Paramjyot Komarjha et al. (2015), A. Yamano et al.(2014)]. As an optical amplifiers and fibers, phosphate glasses have been considered as a promising group of glasses [A.V. Chandrasekhar et al.(2003), Nehal Aboufotoh et al (2014)] and also play an important roles in LASER systems and applications as magneto-optic materials, photonic switching, transmitting optical components and as modulators [D.D. Ramteke et al.(2017)].

Keywords: Phosphate glasses, Structural properties, Optical properties.

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Glasses with specific properties could be achieved by varying glass constituents. Several studies have been shown that a chemical durability of phosphate based glasses can be improved by the addition of various oxides [S.T. Reis et al.(1998), D.E. Day et al.(1998)]. Sodium phosphate glasses have a strong glass forming nature, low crystallization and melting temperatures. It is expected that the replacement of Na₂O by Li₂O in P₂O₅ based glasses exhibit better optical properties and ionic conductivity due to smaller size of Li⁺ (0.76 Å) as compared to Na⁺ (1.02 Å). The structural and physical properties of 55 P₂O₅ – (45-x) Na₂O – x Li₂O glass have been reported recently in our previous work [H.M. Zayed et al.(2018)]. Therefore, it is important to study the effect of the Na₂O and Li₂O modifiers on the optical, thermal stability and crystallization of glass. Recently, the structural and thermal properties of P₂O₅-Na₂O-Li₂O and Li₂O-Na₂O-P₂O doped with La₂O₃ has been reported in literature [Paramjyot Komarjha et al.(2015), A. Yamano et al.(2014), Peipei Chen et al.(2015)]. It was found that the structural properties of P₂O₅-Na₂O-Li₂O glasses strongly depend on Na₂O and Li₂O content.

It was found that in literature the optical properties of P₂O₅-Na₂O-Li₂O glass system have not been studied extensively, for this reason, the present work gives the preparation of 55 P₂O₅ – (45-x) Na₂O – x Li₂O glass containing various concentration of Li₂O reaching to 35 mol% and the investigation of their structural and optical properties.

Experimental

A] Preparation

The investigated glass 55 P₂O₅ – (45-x) Na₂O – x Li₂O (0 ≤ x ≤ 35) were prepared by the conventional melt quenching technique using LiCl as raw material and high purity analytical grade chemicals as (NH₄)₂HPO₄, Na₂CO₃. The appropriate quantity of these chemicals were weighted and mixed thoroughly in agate mortar for about one hour. The batches were initially kept at 400 C° in porcelain crucibles to release volatile products coming from the starting materials and then melted in an electric furnace with intermediate stirring at 1000 C° for one hour to ensure homogeneity of the glasses. Samples of the desired shape were obtained by quenching the melt at 350 C° between two preheated stainless steel plates for two hours to eliminate the mechanical and thermal stresses produced during casting and collected the next day. The prepared glass samples were polished by silicon carbide water proof abrasive papers of various grades ranging between 320 and 1000 to achieve a good optical transparency samples.

B] Density (ρ), molar volume (V_m) and oxygen packing density (OPD)

The density (ρ) of the glass samples was determined at room temperature by the standard Archimedes principle using toluene as an immersion liquid.

C] X-Ray Diffraction measurements (XRD)

The amorphous nature of synthesized glass samples was checked by PANalytical X'Pert PRO diffractometer using CuK α target of wavelength 1.5406 Å and scanning rate 2°/min. XRD patterns were recorded in 2 θ range between 4° and 90°.

D] Differential Thermal Analysis (DTA)

The glass transition temperature (T_g) and the crystallization temperature (T_c), were evaluated for all the glass samples by using SDTQ600 V20.9 and scanned at a heating rate 10 C°/min.

E] Infrared absorption measurements (FTIR)

The infrared absorption spectra of the 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses were measured at room temperature in the wave number range 400 – 4000 cm⁻¹ by a Fourier transform computerized infrared spectrometer type, JASCO, FT/112-43, Japan. The prepared glasses were mixed with KBr in the ratio 2:200 mg glass powder : KBr respectively. The weighed mixture was subjected to a pressure 5 tons / cm² to produce clear homogenous discs. The infrared absorption measurements were measured immediately after preparing the discs.

F] Optical properties

The optical absorption of the glass samples were recorded at room temperature using a double beam Cary 100 spectrophotometer (model UV-12) in the wavelength range 200-900 nm. The uncertainty in the wavelength is found to be ± 1 nm.

Results and Discussion

Density, molar volume and optical packing density

The values of density (ρ) and molar volume (V_m) and oxygen packing density (OPD) have been calculated previously and tabulated in the following **Table 1 [H.M. Zayed et al.(2018)]**.

It was found that the theoretical and experimental values of density decrease with increasing concentration of Li₂O and the molar volume pass through maximum at 15 mol% Li₂O. The density decreases because of substitution of Li₂O of molar mass (29.28 g/mol) instead of Na₂O of molar mass (61.97 g/mol). The experimental density values decreases from 2.962 g/cm³ to 2.361 g/cm³ for the prepared glass by increasing x from zero to 35, also, It could be seen from Table 1 that OPD decreases from 88.3 to 74.3 mole/liter as the concentration of Li₂O increases from zero to 15 mol% indicating that the structure becomes loosely packed with increase of Li₂O content and the formation of a more open macromolecular chain in the prepared glass samples as reported previously [H.M. Zayed et al.(2018)]

Composition of 55 P ₂ O ₅ – (45-x) Na ₂ O – x Li ₂ O x (mol %)	ρ_{exp} (gm/cm ³)	ρ_{the} (gm/cm ³)	V_m (cm ³ /mol)	OPD (mol/litre)
0	2.962	2.81	36.224	88.3391
3	2.668	2.57	39.821	80.3559
10	2.419	2.3	42.911	74.5735
15	2.37	2.27	43.061	74.3139
30	2.364	2.268	40.171	79.66
35	2.361	2.267	39.397	81.2253

Table 1: Experimental density (ρ_{exp}), theoretical density (ρ_{the}), molar volume (V_m) and oxygen packing density (OPD) of different glass compositions.

X-Ray Diffraction measurements (XRD)

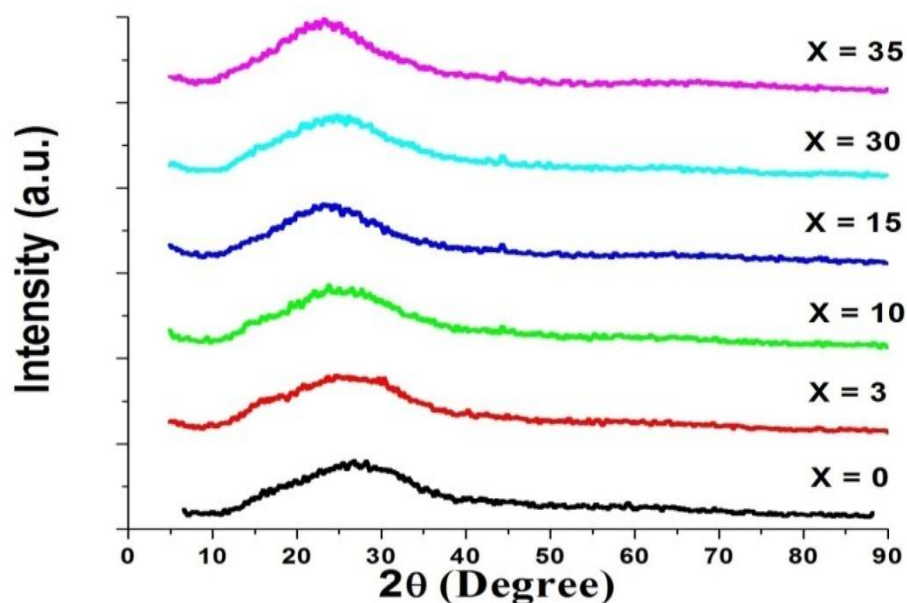


Fig.1. XRD diffraction patterns of 55 P₂O₅ – (45-x) Na₂O – x Li₂O glass samples at different composition of Li₂O (mol.%).

XRD patterns of composition 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses are represented in **Fig.1**. The broad hump presence between 15° and 40° in 2θ range confirming the amorphous nature of the glass. [H.M. Zayed et al.(2018)].

Differential Thermal Analysis (DTA)

The variation of DTA curves of 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses with different concentration of Li₂O mol.% are presented previously [H.M. Zayed et al.(2018)]. The glass transition temperature (T_g) and crystallization temperature (T_c) were found to decrease with increasing of Li₂O concentration except for glass sample with x = 15 mol%. The change of T_c and T_g values with concentration of Li₂O content could be explained on the basis of the nature of bonding present in glass system. **Table 2** reported that the value of glass thermal stability (h') for the glass sample with Li₂O content 15% mol% is found to be maximum, which indicates its highest thermal stability than other glasses.

Composition of				
55 P ₂ O ₅ – (45-x) Na ₂ O – x Li ₂ O	T _g (c ^o)	T _c (c ^o)	ΔT (c ^o)	h' = ΔT/T _g
x (mol %)				
0	234.42	283.56	49.14	0.20962
3	262.13	317.79	55.66	0.21234
10	252.65	310.28	57.63	0.2281
15	285.88	391.05	105.17	0.36788
30	247.52	308.69	61.17	0.24713
35	243.69	305.59	61.9	0.25401

Table 2: Glass transition temperature (T_g), crystallization Temperature (T_c) and glass thermal stability (h') of different glass compositions.

Infrared absorption measurements (FTIR)

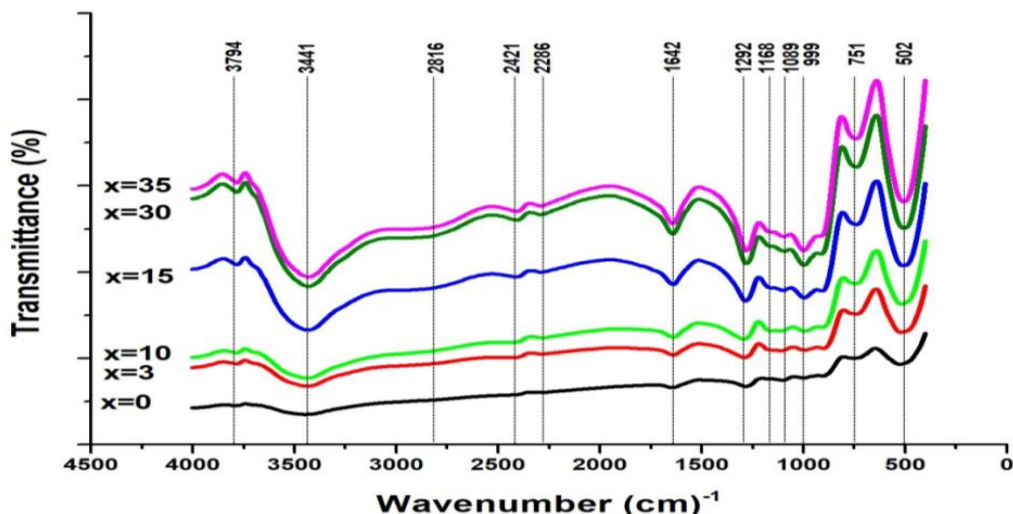
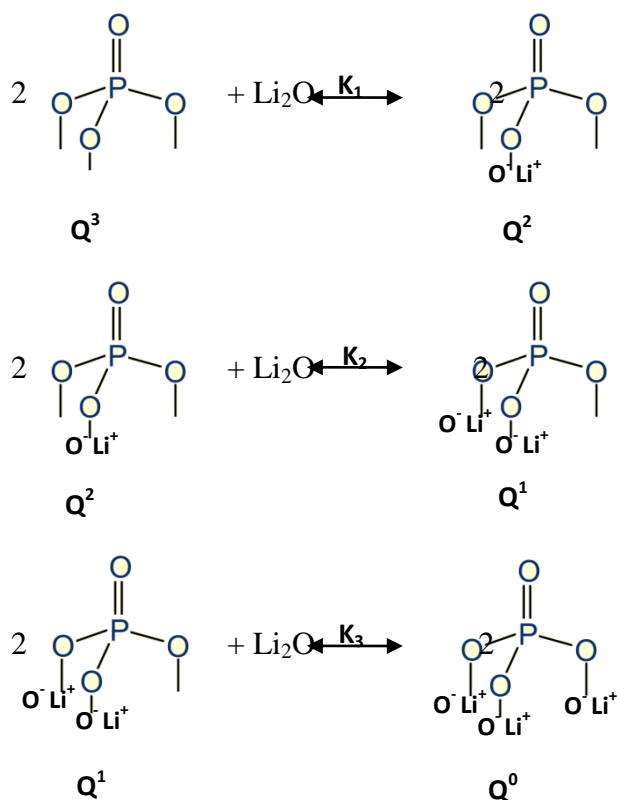


Fig.2. FTIR spectra of the 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses at different compositions of Li₂O (mol.%).

FTIR spectra of 55 P₂O₅ – (45-x) Na₂O – x Li₂O glass is measured in frequency range of 4000-400 cm⁻¹ as shown in **Fig.2**. As the modifier content (Li₂O) increases in glass former (P₂O₅), structural unit of phosphate changes from Q³→Q²→Q¹→Q⁰ according to the following equilibrium equations [**P.K. Jha et al (2015)**].



Where K₁, K₂ and K₃ are the equilibrium constants. This change in structural units from Q³ to Q⁰ provides non-bridging oxygen's which form due to shorten of chain length rigid structures.

It is observed from **Fig.2** that stretching modes (symmetric and asymmetric) shifted to higher frequency as Li₂O mol. % content increase, this may be due to the strengthen of covalent character in glass matrix due to substitution of Na₂O P₂O₅ by Li₂O. The shift of this bands at finger print area (500-800) cm⁻¹ tends to the bending vibration of O=P-O bonds and symmetric stretching group in Q¹ structural units [**Y.M. Lai et al (2011)**, **C. Dayanand et al (1996)**]. The asymmetric stretching vibration in Q² structural unit lies between (800-1000) cm⁻¹ [**G.V. Rao et al (2014)**]. The weak peak at (1000-1100) cm⁻¹ assigned to PO₄³⁻ symmetric stretching group in Q⁰ structural unit [**C. Dayanand et al (1996)**]. Asymmetric stretching modes of PO₂ group in Q² structural unit occur between (1150-1300) cm⁻¹ [**Y. Tsunawaki (1981)**]. H₂O bending vibrations occur in between (1600-2300) cm⁻¹ [**F.H. Elbatal (2011)**]. The shift occurs at higher region (2400-3800) cm⁻¹ may be due to enhancement of OH group. The assignments of the vibrational modes are summarized in **Table 3**.

Wavenumber (cm ⁻¹)						Assignment
x=0	x=3	x=10	x=15	x=30	x=35	
501.8	501.8	501.87	502.2	502.22	502.3	Bending vibration of (O=P-O)
748.5	748.87	749.2	751.15	751.3	751.7	Symmetric stretching of (P-O-P) group in Q ¹ structural unit
998.77	997.77	997.9	999.03	999.4	999.78	Asymmetric stretching of (P-O-P) group in Q ² structural unit
1087.4	1087.53	1088.06	1089.5	1089.9	1089.91	Symmetric stretching of (PO ₄ ³⁻) group in Q ⁰ structural unit
1166.3	1166.5	1167.3	1168.33	1168.77	1168.93	Asymmetric stretching of (PO ₂) group in Q ² structural unit
1641.1	1641.66	1642.1	1642.42	1642.57	1642.64	Bending vibration H ₂ O molecule
2285.05	2285.44	2286.03	2286.18	2286.3	2286.7	Bending vibration H ₂ O molecule
3440.2	3440.73	3440.99	3441.23	3441.62	3441.98	Oscillations due to symmetric stretching of O-H group

Table 3: FTIR bands for 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses of different glass compositions.

Optical properties

Optical measurements are powerful tool for band structure discussion and calculating the band gap width, also, optical parameters of both ordered and disordered materials. **Fig.3** shows the measured absorbance for 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses. Absorption coefficient (α) is measured according to the following relation:

$$\alpha(\nu) = (1/t) \ln (1/T) = (1/t) \ln A$$

Where, T is the transmittance, t is the thickness of the glass sample and A is the absorbance.

The absorption coefficient (α) for the glass samples with different concentration has been calculated and plotted as shown in **Fig.4**.

The relationship between the absorption coefficient and the incident photon energy ($h\nu$) is presented according to the following relation [**J.I. Pankove (1971), J. Tauc (1974)**]:

$$\alpha(\nu) = K \cdot \alpha(h\nu - E_g)^n / h\nu$$

Where, K is constant dependent on transition probability, E_g is the band gap width and n is an index that characterizes the process of optical absorption in investigated glasses and equal to 2, 1/2, 3, 3/2 for an indirect allowed, direct allowed, indirect forbidden and direct forbidden transition respectively [**A.F. Qasrawi (2005)**].

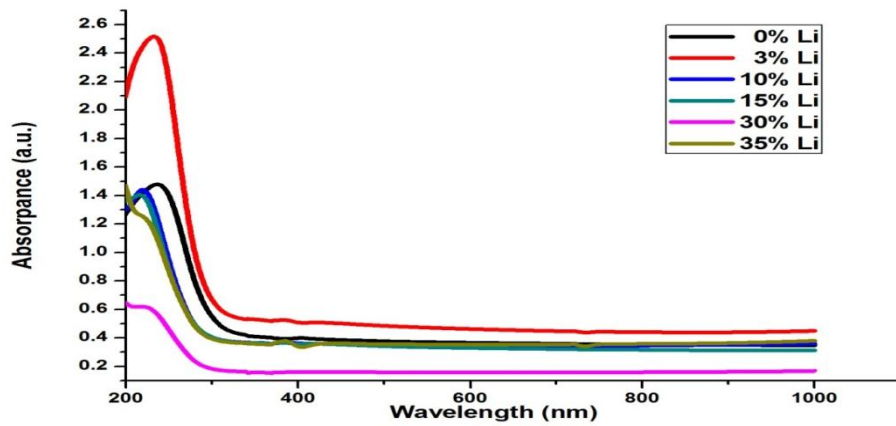


Fig.3. Absorbance spectra of the 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses at different compositions of Li₂O (mol.%).

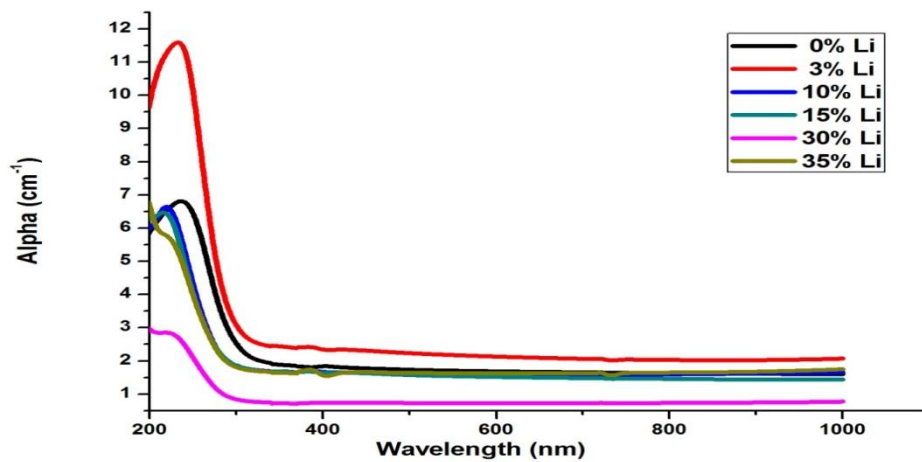


Fig.4. Absorption coefficient of the 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses at different compositions of Li₂O (mol.%).

Amorphous materials such as glasses is usually corresponding to the indirect transition, so, $h\nu$ was plotted against $(\alpha h\nu)^{1/2}$ in **Fig.5** for 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses.

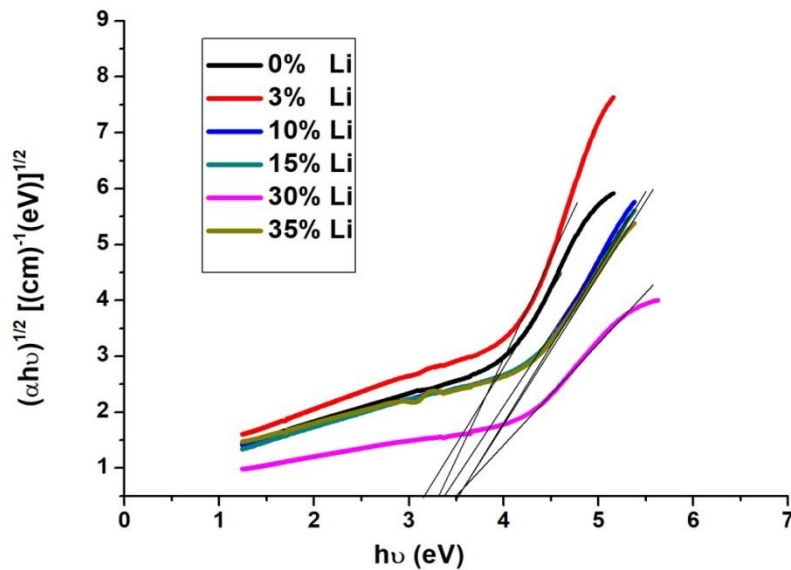


Fig.5 Variation of $h\nu$ against $(\alpha h\nu)^{1/2}$ for 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses at different compositions of Li₂O (mol.%).

At high absorption regions, optical band gap energy was calculated by doing a linear fitting for each curve in **Fig.5** and the intersection on $h\nu$ axis gives the corresponding optical band gap energy E_g .

The Urbach energy which is the width of the tail of localized states in band gap could be calculated according the following equation:

$$\alpha = \text{constant} \cdot \exp(h\nu/E_u)$$

$$\ln(\alpha) = (h\nu/E_u) - \text{constant}$$

In the present study, Urbach energy could be presented in **Fig.6** for 55 P₂O₅ – (45-x) Na₂O – x Li₂O glasses at different compositions of Li₂O (mol.%). It is found that the energy gap (E_g) increases from 3.2 eV to 3.5 eV by increasing Li₂O mol. % content and Urbach energy decreases from 1.133 eV to 0.838 eV as presented in **Fig.7**.

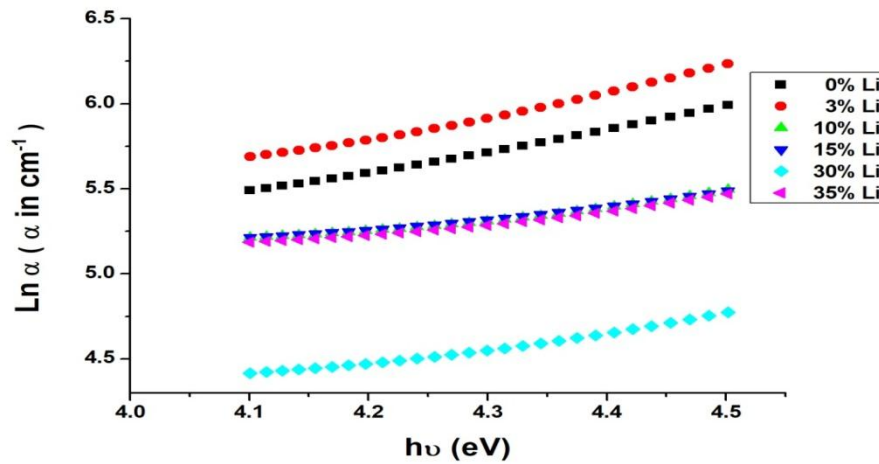


Fig.6 $\text{Ln } \alpha$ versus $h\nu$ for $55 \text{ P}_2\text{O}_5 - (45-x) \text{ Na}_2\text{O} - x \text{ Li}_2\text{O}$ glasses at different compositions of Li_2O (mol.%).

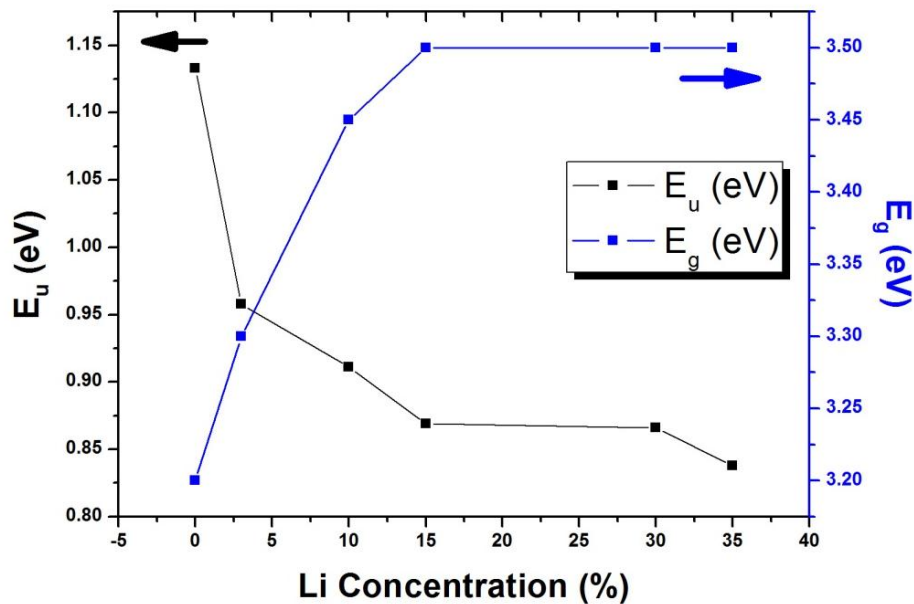


Fig.7 Optical energy gap and Urbach energy versus glass composition for $55 \text{ P}_2\text{O}_5 - (45-x) \text{ Na}_2\text{O} - x \text{ Li}_2\text{O}$ glasses at different compositions of Li_2O (mol.%).

Conclusion

All the prepared glass samples are amorphous in nature as confirmed by XRD. The experimental and theoretical densities are found to decrease with increasing Li_2O content, and following the same trend, while the molar volume (V_m) has opposite trend with the concentration of Li_2O . The glass transition temperature (T_g) and crystallization temperature (T_c) were found to decrease with

increasing of Li₂O content except for glass sample with x = 15 mol%, this glass sample exhibit the highest thermal stability. The FTIR of the prepared glasses were investigated. The variation of optical absorption edge, optical band gap (E_g) and Urbach energy (E_u) depend on Li₂O content. It is observed that the increasing of Li₂O content increases the energy gap values and decrease the Urbach energy which is an indication of the increase in structural disorder of glass.

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الملخص باللغة العربية

دراسة الخواص الضوئية لزجاجيات فوسفات الصوديوم المعدلة بأكسيد الليثيوم

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فى هذا البحث تم دراسة زجاجيات $55 \text{ P}_2\text{O}_5 - (45-x) \text{ Na}_2\text{O} - x \text{ Li}_2\text{O}$ حيث ان $(0 \leq x \leq 35)$ ، و قد تم فحص الزجاج المحضر باستخدام تقنية حيود أشعة اكس (XRD) و التحليل الحرارى التفاضلى (DTA) و الامتصاص الضوئى للأشعة المرئية و الفوق بنفسجية (UV-VIS optical absorption) و قياسات تحول فوربييه للأشعة تحت الحمراء (FTIR)، كما تم دراسة التحليل الحرارى التفاضلى (DTA) و كذلك تم حساب قياسات الكثافة (ρ) و كثافة الحزمة الأوكسجينية (OPD) و الحجم المولارى (V_m)، و قد تم قياس الامتصاص لهذه الزجاجيات و الذي استخدم لحساب معامل الامتصاص الضوئى و طاقة الفراغ الضوئى. و اثبتت الدراسات الضوئية أن طاقة الفراغ الضوئى الغير مباشر (E_g) تزيد من 3.2 eV الى 2.5 eV و أن طاقة أوربخ تقل من 1.133 eV الى 0.838 eV مع زيادة تركيز Li_2O .