Characterization of some lead vanadate glasses

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ABSTRACT

Studies on lead vanadate glasses modified with Li_2O have been carried out. Elastic properties and Debye temperature have been investigated using sound velocity measurements at 4 MHz. The ultrasonic and the IR spectroscopic studies have been employed to investigate the structure of lead vanadate glasses in the presence of Li_2O. IR analysis indicates that increasing the vanadate content causes a shift of the bands to higher wave number and to higher relative area which was attributed to the higher dissociation energy of V_2O_5 than that of PbO. Thus, the average force constant of VO_5 structural units increases with increasing V_2O_5 content. The change of density and molar volume with V_2O_5 content reveals that the decrease in density is related to the replacement of high dense PbO with low dense one V_2O_5, where the increase in the molar volume can be attributed to the larger packing factor of V_2O_5 than that of PbO. The observed compositional dependence of the elastic moduli is interpreted in terms of the effect of V_2O_5 on the coordination number of the vanadate and lead structural units.

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1. Introduction

The structural chemistry of crystalline oxides such as PbO and V_2O_5 revealed that the structure of V_2O_5 is built of octahedrons, where the pentavalent V has 5-coordination with oxygen atoms. Although V^v thus behaves like P^v in forming the ions $VO_4{}^{3-}$ and $V_2O_7{}^{4-}$ it shows a much greater tendency than P to form condensed oxy-ions. On the other hand, among the various lead oxides, the tetragonal PbO has a layer structure in which the metal atom is bonded to 4 O atoms which are arranged in a square to one side of it, with the lone pair of electrons presumably occupying the apex of the tetragonal pyramid. The structure is built of layers having four bonds two of them have lengths 2.20 Å and the other two have lengths 2.49 Å. The shorter bonds delineate zigzag chains which are bonded into layers by the longer Pb—O bonds [1–2].

On the other hand, the V_2O_5-rich glasses in which V_2O_5 acts as the network former have the network structure mainly consisting of corner-sharing branched VO_4 tetrahedra of the same structural units as found in phosphate glasses. The network structure was reported to be made up of unaffected VO_5 groups as in vitreous V_2O_5 and affected VO_5 groups with alkaline earth ions in contrast to the vanadate glasses formed by conventional network formers in which only unaffected VO_5 groups are present [3–9]. These glasses are known to contain V^{4+} and V^{5+} ions where the electrical conduction was attributed to the hopping of $3d^1$ unpaired electron from V^{4+} to V^{5+} site which induces a polarization of the vanadium ion around it and forms a polaron [10–15].

Among vanadate glasses lead vanadate has received greater attention as a new branch in semi-conducting glasses because of its wider glass-forming region in the phase diagram [16], and its possible technological applications in threshold switching [17], memory switching [18], electrical threshold, electrochemical batteries [19], and optical switching devices. The PbO:V_2O_5 in 1:1 molar ratio is at the eutectic composition giving a stable metavanadate (PbV_2O_6) crystalline phase with known crystal structure [20–21]. The local structure of binary lead vanadate glasses as a function of PbO composition has been studied by a variety of techniques which concluded that two different forms of metal ion distribution in the glasses in relation to vanadium–oxygen polyhedra, and Pb^{2+} ion occupies the interstitial position like many other divalent ions like Zn^{2+}, Cd^{2+}, etc. Accordingly, the basic structural units were identified as unaffected VO_5 trigonal bipyramids as in crystalline V_2O_5, affected VO_5 groups as in crystalline $Pb(VO_3)_2$, V_2O_7 pyrovanadate units and VO_4 tetrahedra which are composed of $V_2O_7{}^{4-}$, $(VO_3)_n$ single chains, branched VO_4, and $(V_2O_8)_n$ zigzag chains depending on the PbO content [22–28].

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In literature, there are a few studies on ternary and quaternary vanadate glass systems such as V_2O_5–BaO–ZnO glass system [29–31], or La_2O_3 and Fe_2O_3 are added to PbO–V_2O_5 glass system [32]. Lee et al. [33] assumed that oxide Li^+ conducting glass is a promising candidate for the electrolyte materials of thin-film batteries because it exhibits an isotropic ionic conduction and stability at a high voltage. The authors [33] found that the ionic conduction is more improved in the case of Li_2O—B_2O_3—V_2O_5. On the other hand, Garbarczyk et al. [34] found that glasses of the Li_2O–V_2O_5–P_2O_5 system transformed into nanomaterials via annealing at crystallization exhibit much higher electrical conductivity and are thermally stable to higher temperature than the initial glasses. Therefore, in the present investigation, an attempt has been made to explore the elastic constants and their influence on the structure of the pseudo binary system $5Li_2O$–$(45 − x)PbO$–$(50 + x)V_2O_5$ ($x = 0, 5, 10,$ and 15 mol.%) employing the FTIR and ultrasonic studies.

2. Experimental procedures

The glass samples having the general chemical formula $5Li_2O$–$(45 − x)PbO$–$(50 + x)V_2O_5$ with $x = 0, 5, 10,$ and 15 mol.% have been prepared by the melt quenching technique. Required quantities of Analar grade Li_2CO_3, PbO, and V_2O_5 were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture was melted in a porcelain crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1123–1173 K (according to PbO content) for 2 h to homogenize the melt. The glass formed by quenching the melt on a preheated stainless-steel mold was immediately transferred to another furnace where it was annealed at 493 K for 1 h. The composition given in Table 1 refers to the nominal composition (the starting mixture), where the weight losses were found to be less than 0.5%. The cylindrical glass samples, 1 cm length and 1 cm diameter, are obtained by pouring the melts in a cylindrical Cu mould. The obtained glasses were lapped and two opposite sides were polished to be suitable for the use in the ultrasonic velocity measurements. Non-parallelism of the two opposite side faces was less than 0.01 mm.

X-ray measurements were recorded to check the non-crystallinity of the glass samples using a Philips X-ray diffractometer PW/1710 with Ni-filtered, Cu Kα radiation ($\lambda = 1.542$ Å) powered at 40 kV and 30 mA. The XRD patterns (not shown) showed that the glasses did not reveal discrete or any sharp peaks, but the characteristic broad humps of the amorphous materials.

The infrared absorption spectra of the glasses in the wave number range of 400–2000 cm^{-1} with a resolution of 4 cm^{-1} were measured at room temperature by an infrared spectrophotometer type JASCO, FT/IR–430 (Japan), using the KBr pellet technique. The infrared spectra were corrected for the dark current noises, and normalized to eliminate the concentration effect of the powder sample in the KBr disc. The resulted spectra are deconvoluted to enable us to shed further light on the structural units consisting the glass.

The density (ρ) of the glass samples was determined using Archimedes technique by using toluene as the worked fluid. The accuracy of the measurements was ±15 kg m^{-3}. The molar volume (V_m), and the mean atomic volume (V_a), have been determined as M/ρ, and V_m/q, respectively, where M is the molar weight of the glass calculated by multiplying x times the molecular weights of the various constituents, and q is the number of atoms in the unit formula.

The ultrasonic velocities [longitudinal (v_L) and shear (v_T)] at room temperature (300 K) were obtained by using the pulse-echo method. In this method, x-cut and y-cut transducers (KARL DEUTSCH) operated at a fundamental frequency 4 MHz, and a digital ultrasonic flaw detector (KARL DEUTSCH Echograph model 1085) were used. The uncertainty in the measurement of the ultrasonic velocity is 10 m s^{-1}. The two velocities besides the density were utilized in determining two independent second-order elastic constants (SOECs), namely, the longitudinal (C_{11}) and shear (C_{44}) moduli. C_{11} and C_{44} described the elastic strain produced by a small stress in an isotropic amorphous solid like glasses. For pure longitudinal waves $C_{11} = \rho v_L^2$, and for pure transverse waves $C_{44} = \rho v_T^2$. The elastic bulk modulus (K_e), Young·s modulus

(Y), the Debye temperature (θ_D) and Poisson·s ratio (σ) can be determined from C_{11} and C_{44} using the standard relations adopted in previous work [35].

3. Results and discussion

3.1. Infrared spectral studies

To get more information about the structural changes that take place in the studied glass network, some features of the stoichiometric lead vanadate glass (PbO:V_2O_5 in 1:1 molar ratio) should be taken into account [20–21]. Following the work of Dimitrov [24,26] on the structural interpretations of vanadate and tellurite glasses as non-conditional glass-formers, it was assumed that there was a similarity between the spectra of amorphous and its crystalline counterpart which is direct proof for the similarities of the structural units and of the short range order. Also, according to an assumption in vibrational spectroscopy of the solid-state [36–37], the vibrations of a specific group of atoms in a lattice may be regarded as relatively independent from motions of the rest of the atoms. Accordingly, the IR spectrum of vitreous V_2O_5 is similar to that of the crystal and shows a band at 1020 cm^{-1} [9]. This fact means that the isolated V═O bonds from the VO$_5$ trigonal bipyramids are preserved in the vitreous structure. The main coordination polyhedron for vanadium in the crystal structures is the VO$_4$ tetrahedron with three terminal V—O bonds forming VO$_3$ groups. In the vitreous V_2O_5 counterpart, there is a band at around 920 cm^{-1} is close to the symmetrical stretching vibration of VO$_3$ unit, in the spectra of crystals. The band at 800 cm^{-1} falls in the range of the antisymmetric stretching vibrations of VO$_3$ unit [26,38]. Hayakawa et al. [39], and Ramesh and Sastry [40] studied the crystalline and amorphous lead vanadate glasses by IR spectroscopy, and found that the observed bands at 820–956 cm^{-1} are assigned to the two types of stretching vibration such as $v(VO_3)$ and $v(VO_2)$ indicating that the glass network consists of VO$_4$ tetrahedra constituting $V_2O_7^{4-}$ or $(VO_3)_n$ single chain. The high-frequency bands at 950–970 cm^{-1} are attributable not only to the VO$_5$ groups but also to the branched VO$_4$ groups having one V═O double bond.

The observed broadening of the bands in the spectra of the studied glasses may be due to two reasons. The first reason is the distribution of bond-angles and lengths and the fluctuation of the local electronic and atomic environments in the amorphous state which results in a spectra similar to the spectra of the crystalline phases. The second reason, according to the bases of the solid-state physics is the break down of wave vector selection (k-selection) rules in amorphous as a consequence of disorder when compared to crystalline forms, which allows electromagnetic radiation to couple with vibrations other than $k = 0$. As a result, unlike the crystalline case in which narrow well defined lines are observed, broad and diffuse bands representing a continuum of IR absorption result. Even though bands due to individual, localized structural units are observable, the identification of IR spectra of glasses alone is rather difficult unless crystalline spectra are also present [40]. Accordingly, the broad band of amorphous state is the overlapping of some individual bands with each other. Each individual band has its char-

Table 1
The composition of the glass system $5Li_2O$–$(45 − x)PbO$–$(50 + x)V_2O_5$ glasses, their nominations, density (ρ), the molar volume (V_m), the packing density (V_t), longitudinal (v_L) and shear (v_T) ultrasonic velocities, Poisson's ratio, the elastic moduli; Young's modulus (Y), shear modulus (G), bulk modulus (K), the ratios (d), and C_{44}/C_{12} and the fugacity (f_g).

Nomination Gx	Composition in mol %			ρ (kg m^{-3})	$V_m \times 10^{-6}$ (m^3 mol^{-1})	V_t	v_L (m s^{-1})	v_T (m s^{-1})	σ	Y (Gpa)	G (Gpa)	K (Gpa)	(d)	C_{44}/C_{12}	f_g
	V_2O_5	Li_2O	PbO												
G1	50	0	50	5080	39.87	0.576	3510	1830	0.313	44.69	17.01	39.90	1.71	0.596	0.012
G2	50	5	45	4820	40.02	0.570	3560	1870	0.309	44.14	16.86	38.61	1.75	0.616	0.013
G3	55	5	40	4700	40.60	0.591	3580	1885	0.308	43.70	16.70	37.97	1.76	0.622	0.013
G4	60	5	35	4530	41.67	0.604	3620	1910	0.307	43.20	16.53	37.33	1.77	0.628	0.013
G5	65	5	30	4380	42.62	0.618	3660	1935	0.306	42.84	16.40	36.81	1.78	0.634	0.014
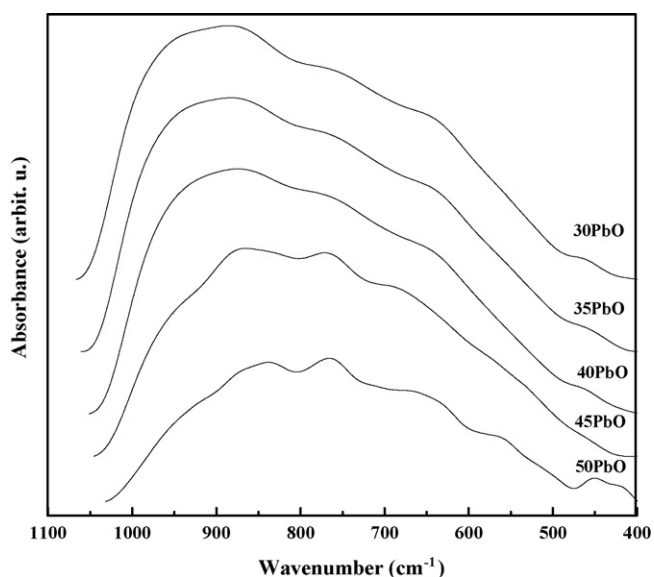
Fig. 1. Infrared absorption spectra of $5Li_2O–(45 − x)PbO–(50 + x)V_2O_5$ glasses.

Table 2
Deconvolution parameters of the infrared spectra of glasses G1–G5. C is the component band center and A is the relative area (%) of the component band.

G1	C	440	549	665	777	830	867	929	980
	A	2.2	9.1	29.4	26.1	3.2	14.2	13.2	2.61
G2	C	468	544	684	773	–	871	957	993
	A	0.3	7.3	30.7	28.7	–	24.8	6.4	1.8
G3	C	460	532	635	779	–	891	954	993
	A	1	3.3	21.9	38.8	–	21.6	9.9	3.5
G4	C	458	532	630	774	–	893	959	1000
	A	0.8	3.9	18.1	39.7	–	22.9	10.6	4
G5	C	460	543	628	776	–	895	965	1007
	A	0.7	4.9	12.2	41.8	–	25	11.2	4.2

acteristic parameters such as its center (C), which is related to some type of vibrations of a specific structural group, and its relative area (A), which is proportional to the concentration of this structural group.

A deconvolution process, as described elsewhere [41], should be performed to get such parameters. Therefore, the systematically changes in the infrared spectra of the glasses under study showed the presence of three principle broad bands at around 450, 750 and $850 cm^{-1}$, as shown in Fig. 1. The spectra showed a shift towards higher wave numbers in the three principal bands as the PbO. Fig. 2 shows the deconvolution of the spectrum of the glass sample G3. The deconvolution parameters of the bands for the investigated glasses are given in Table 2.

There is a good agreement between the data of sample having 0 mol.% Li_2O content and those from the literature [39–40] concerning the IR spectra of the lead vanadate glasses. The bands at around 440–467 and 532–549 cm^{-1} are attributed to the vibrations of angular deformation vibration of the O—V bond [42]. According to the expected wave number of Pb—O derived from the crystalline PbO [1], and according to another work elsewhere [43], the band at around 532–549 cm^{-1} may be overlapped with that attributed to the deformation vibrations of the Pb—O. The bands around

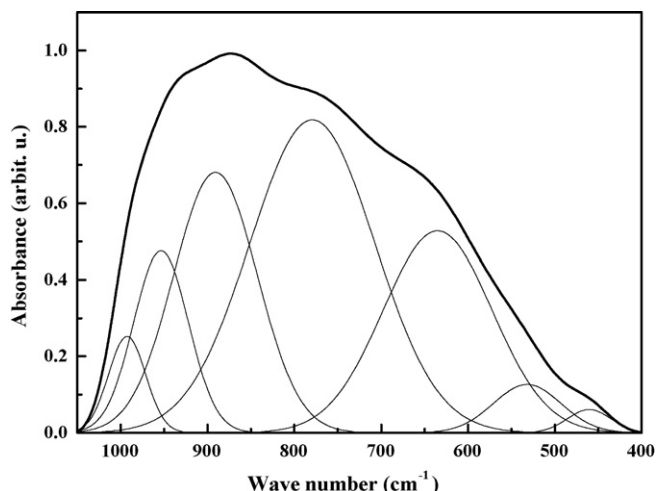665–628 cm^{-1} are assigned to combination vibrations of $(VO_3)_n$ single chain [39–40] or due to antisymmetric vibrational modes of V—O—V group [42]. The bands around 760–779 cm^{-1} are attributed to the bending frequency while the bands around 830–895 cm^{-1} are attributed to the asymmetric vibrations of $\nu(VO_2)$ and $\nu(VO_3)$ respectively [40]. The bands around 929–1007 cm^{-1} are attributed to the symmetric stretching vibrations [42].

Insertion of Li_2O on the expense of PbO leads to a shift of the IR bands of the base glass (stoichiometric lead vanadate glass) to higher wave number and lower relative area. This could be attributed to the higher bond strength and lower ionic radii of Li_2O than that of PbO. On the other hand, the packing density and the dissociation energy of Li_2O and PbO are 9 and $11.1 \times 10^{-6} m^3 mol^{-1}$, and 77.9 and $25.3 \times 10^9 J m^{-3}$, respectively [44]. The Li^+ ions, accordingly can occupy an interstitial position in the lead vanadate glasses, and enhance the stretching of vanadate glasses as suggested before [43]. This mechanism is in contrast with the suggested mechanism for binary divalent vanadate glasses [9,26]. Increasing the vanadate content, at constant Li_2O content, on the expense of PbO content causes the principal bands of vanadate to shift to higher wave number and to higher relative area. It is reasonable as the dissociation energy (bond strength) of V_2O_5 is higher than that of PbO [44]. This is in accordance with the increase in the vanadium ion density from 1.51 to $1.84 \times 10^{28} m^{-3}$. The average force constant of VO_5 structural according to Table 1 increases units with increasing V_2O_5 content. The average force constant was determined according to elsewhere work [45]. This increase can be attributed to the higher bond strength of V_2O_5 than that of PbO, and to the higher coordination number (5) of V_2O_5 than that of PbO (4) which increase the number of bonds per unit volume [1]. Thus, the connectivity of the structure will increase, which reveals the former role of V_2O_5 in the studied glasses.

Also, the shift of IR bands is found to be in a good agreement with the suggestions of Mekki et al. [46], as the decrease in PbO content beyond 0.5 mol leads to the transformation of its former role to modifier role. So, as PbO content decreases, the non-bridging oxygens will be converted to bridging one which increases the connectivity as discussed before.

3.2. Density, and molar volume

On the other hand, the density is a powerful tool capable of exploring the changes in the structure of glasses. The density is affected by the structural softening/compactness, change in geometrical configuration, coordination number, cross-link density and dimension of interstitial spaces of the glass.

In the studied glasses, it is noted that, the density decreases from 5080 to 4380 $kg m^{-3}$, congruent with an increase in the molar volume from 39.9×10^{-6} to $42.6 \times 10^{-6} m^3 mol^{-1}$ as the V_2O_5 content increases on the expense of PbO content as shown in Fig. 3, and listed in Table 1. The density value of 50 PbO–50 V_2O_5 glass
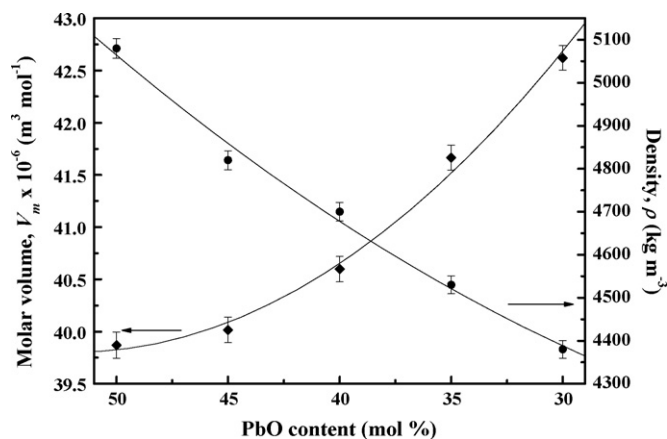

Fig. 2. Infrared absorption spectra of $5Li_2O–40PbO–55V_2O_5$ glasses.

Fig. 3. Dependence of the density and the molar volume of on the percentage of PbO content.

Fig. 4. Dependence of the ultrasonic velocity and Debye temperature in on the percentage of PbO content.

agrees well with that reported elsewhere [39,47]. The density values of the studied glasses are greater than the density value for pure V_2O_5 (2960 kg m^{-3}) [48] and agree with a reported data elsewhere [39,47]. The decrease in the density is related to the replacement of high dense PbO (9350 kg m^{-3}) with low dense one V_2O_5 (3350 kg m^{-3}) or Li_2O (2013 kg m^{-3}), i.e., the decrease in the density is related to the constitution of the glass.

In general, it is expected that the density and the molar volume should show opposite behavior to each other, and so in the studied glasses the molar volume increases with the decrease in the density as the PbO content increases, as shown in Fig. 3 and listed in Table 1. The increase in the molar volume can be attributed to the larger packing factor of V_2O_5 (1.89) than that of PbO (0.27). The packing factor of Li_2O is 0.12 (its content is constant in the studied glass system). The packing factor was calculated according another work [49]. Accordingly, the structure of the studied glasses will be expanded, but with compactness and high number of covalent bonds with an increase in the number of bridging oxygens. The compactness is evident from the increasing of the packing density as listed in Table 1, and the increase in covalent bonds and bridging oxygens are evident from the IR analysis as the PbO content decreases. This mechanism is in the contrary to the explanation of the expansion of the molar volume of many glass systems.

3.3. Ultrasonic and elastic behaviour of glass

The values of longitudinal and shear ultrasonic wave velocities with modifier mol % content are listed in Table 1. According to Table 1 and Fig. 4, it was found that the ultrasonic velocities, Debye temperature (θ_D), and increase in the studied glasses with a decrease in Poisson's ratio as the V_2O_5 content increases. The behaviour of Y and L is shown only in Fig. 5 as the behaviour of G and K is similar to those of Y and L in all glasses. As seen from Fig. 5 all the elastic moduli values decrease as the V_2O_5 content increases. The values of the ultrasonic parameters of the sample G1 in a good agreement according to an earlier work [47].

The observed increase in the ultrasonic velocity can be explained by two approaches. The first one is the assumption that, increasing the vanadate content on the expense of PbO will increase the covalent bonds and also the bridging oxygens. Thus, some ionic bonds as Pb—O—V will be transformed into V—O—V covalent bonds. Also, the Li$^+$ may be inserted interstitially into the lead vanadate glasses due to its smaller radii than the others which contributes into the increase in the packing density. Thus, compactness will increase which enhance the rigidity of the glass. These reasons according to IR analysis will contribute to the increase in the ultrasonic velocity. The second approach is the suggestions put forward by Higazy
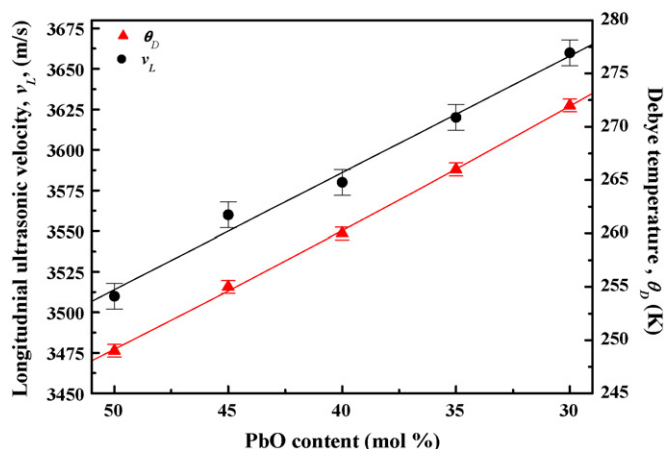
and Bridge [45], where the longitudinal strain in a bond is directly dependent on the bond stretching force constant. In the studied glasses, the longitudinal strain in the main chains (V–O–V linkages) is affected with the former role of V_2O_5, as its increasing content with its high bond strength than that of PbO will increase the overall stretching force constant ($F_{B–O}$), as observed from IR spectra, so the longitudinal wave velocity will increase. On the other hand, the shear strain changes with the bond bending force constant (F_b). Thus, the increase of the shear wave velocity indicates that the decrease in PbO content has a pronounced bending effect on the behaviour of bond bending force constant, as its relative area according to IR analysis increases, i.e., the decrease in the PbO cations will contribute to fill the network interstices.

Debye temperature (θ_D) plays an important role in solid materials in the determination of elastic moduli and atomic vibrations. θ_D represents the temperature at which all the low-frequency 'lattice' vibrational modes are excited. It is known that Debye temperature depends directly on the mean ultrasonic wave velocity [35,45], so Debye temperature increases as the V_2O_5 content increases as shown in Fig. 4. The increase in θ_D can be explained by taking into account two factors. The first is the clear shift of the vibrational modes in the IR absorption spectra [the region around 950 cm^{-1}], as shown in Fig. 1, towards higher wave numbers with increasing the V_2O_5 content. The second is the change in the relative strength of bonds in the glass network as discussed before.
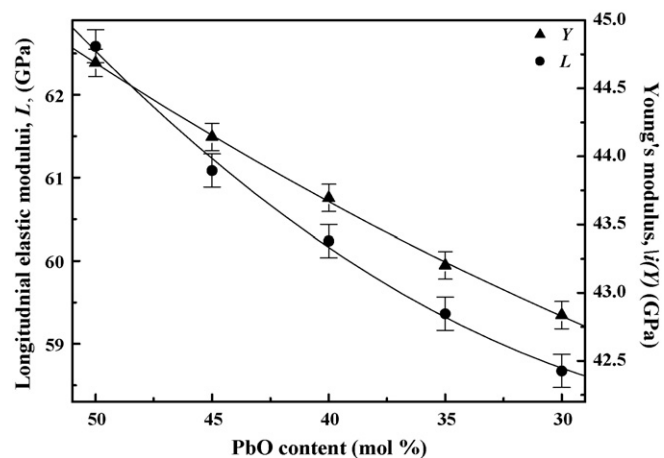

Fig. 5. Dependence of the longitudinal elastic moduli and Young's modulus on the percentage of PbO content.

According to Rao [2], Poisson's ratio depends on the dimensionality of the structure and cross-link density. A three-dimensional network structure (e.g., SiO_2 or GeO_2) has lower σ value than that of a two-dimensional structure (e.g., B_2O_3 or P_2O_5), since the number of bonds resisting a transverse deformation decreases in that order. Increasing of V_2O_5 content on the expense of PbO results in a decrease of σ which is due to the transformation of VO_4 structural units in to VO_5 structural units and the increase in the average cross-link density from 2.67 to 2.77, thus an increase in the dimensionality will occur. On the other hand, the increase in the cross-link density is attributed to the change in the type of bonding from ionic bonds exist in the stoichiometry of lead vanadate glass to covalent ionic bonds as the vanadate network starts to be strengthened as discussed before.

The amorphous structure can be described by two parameters [50–51], one of them is the ratio (d), defined as the degree of the dimensionality of amorphous structure. Hwa et al. [50] proposed that, this ratio equals to $4C_{44}/K_e$. This ratio is 3 for the three-dimensional tetrahedral coordination polyhedron (e.g., pure vitreous SiO_2), while two-dimensional layer structures have $d = 2$. The second parameter given by Chen et al. [51] is the ratio C_{44}/C_{12}, $C_{12} = C_{11} - 2C_{44}$. The authors [51] claimed that, this ratio is considered as an indicator of the character of the force field. It was observed that, $C_{44}/C_{12} = 1$ when the type of the forces is central and $C_{44}/C_{12} \neq 1$ if the type of forces is non-central. It was found that, as the ratio of C_{44}/C_{12} approaches to unity; the central force field may reduce the fraction of the broken bonds in the glass structure.

In the investigated glasses as the V_2O_5 content increases, it was noted that the two ratios describing the dimensionality of the amorphous structure increase, from 1.71 to 1.78 for (d) and from 0.59 to 0.63 for (C_{44}/C_{12}), respectively. The increase in the two ratios is attributed to the increase in the dimensionality which is a direct result of the increase in the average cross-link density as the V_2O_5 increases. Table 1 collects the values of the two ratios (d) and C_{44}/C_{12} of the studied glasses. Accordingly, the structure of the studied ternary lead vanadate glasses, have two-dimensions and the predominant forces are non-central, which result from the ion-overlapping and covalent bonding.

Another important parameter in this study is the fluctuation free volume (fugacity f_g) which plays an important role in the molecular kinetic process in liquids. The viscosity of the inorganic glasses and their structural features can be described using mathematical formulation proposed by Ferry [52]. Sanditov et al. [53] suggested that, formation and migration of micro-cavities in silicate glasses are associated with the deformation of the silicon–oxygen network as a result of thermal fluctuations. The proportion of free volume at the glass transition temperature (fugacity) characterizes the degree of rigidity of the glass network. Fugacity is calculated from the equation given by [52] as;

$$f_g \ln\left(\frac{1}{f_g}\right) = \frac{(1 - 2\sigma)^2}{2(1 + \sigma)} \tag{5.1}$$

where σ is Poisson's ratio. It was observed from Table 2 that values of fugacity increase as the V_2O_5 content increases. The fugacity for pure vitreous TeO_2 and SiO_2 is 0.034, and 0.078, respectively, while for binary tellurovanadate glasses seems to be about 0.01 and for ternary tellurite glasses is almost 0.042 [54]. This variation in the fugacity trend can be correlated to the two-dimensional structure of the lead vanadate glasses as discussed before.

In solids, the crystal lattice is represented by a gas of interacting phonons of energy $\hbar\omega$, where ω is the frequency of a lattice mode. In this picture the ultrasonic wave is composed of very many low-frequency phonons at the ultrasonic frequency. On the other hand, the elastic properties of the glasses are of interest because
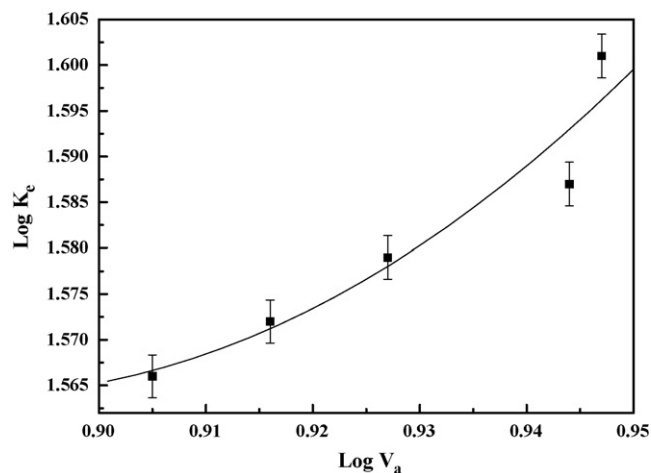

Fig. 6. Variation of the bulk modulus with the values of the mean atomic volume of the lead vanadate glass system in (log–log) representation.

they characterize anharmonic properties, that is, the non-linearity of the atomic displacements. The anharmonicity of a glass, in general, is closely correlated with the fragility of its liquid phase, i.e., fragile as opposed to strong glass-formers should have an overall larger anharmonicity regulating their vibrational properties. Also, the vibrational anharmonicity of the acoustic modes of borate-based glasses can be ascribed to their low coordination and relative ease of bending vibrations [54–56].

Therefore, the compositional dependence of the elastic properties of the studied glasses can be interpreted through two approaches. The first one is related to the relatively large electron-phonon anharmonic interactions results from the increasing of V_2O_5 on the expense of PbO content. Existence of the created bridging oxygens, will affect the variation of the anharmonicity of lead vanadate glasses, as weighed by variation of bonds from ionic bonds to covalent bonds characterize the vanadate based glasses. These factors will enlarge the amplitudes of the oxygen vibrations which result in the appearance of the anharmonic effects. Oxygen is taken into consideration because of its smaller mass than the masses of the various cations.

The second approach can be explained by taking into account the relation between the bulk moduli and the mean atomic volume V_a. The bulk modulus (K_e) and the mean atomic volume (V_a) are related by the relation; $K e V_a^m = C$ [57] (where C is a constant). As stated earlier, the value of m for oxide glasses is 4 [58], and the variation of m in the bulk modulus–volume relationship is determined by the nature of the bonding, and the coordination polyhedra. When the volume change occurs without change in the nature of the bonding or change in the coordination polyhedra, the $\log(K_e)$–$\log(V_a)$ plot in general will be linear. Thus, the $\log(K_e)$–$\log(V_a)$ plot for the investigated glasses as shown in Fig. 6, shows an increase in the mean atomic volume associated with an expected decrease in the bulk moduli. It is clear from the above results that the type of bonding, the coordination states of the various oxides incorporated in the borate network play a dominant role in determining the bulk modulus rather than the volume (i.e., density). The observed decrease in the bulk modulus is associated with a decrease in the number of bonds per unit glass formula unit. The bulk modulus of a covalent network is determined by the bond density (number of bonds in a unit volume), and by the stretching force constant. The force constant is related to the cation field strength of the modifier, i.e., high field strength cations polarize their environment strongly and enhance the ion-dipole interaction.

4. Conclusions

Elastic properties, and IR studies on $5Li_2O–(45-x)PbO–(50+x)V_2O_5$ ($x = 0$, 5, 10, and 15 mol.%) glass system have been investigated to explore the structure of lead vanadate glasses in the presence of Li_2O. IR analysis indicates that increasing the vanadate content causes a shift of the bands to higher wave number and to higher relative area which was attributed to the higher dissociation energy of V_2O_5 than that of PbO and to the presence of Li_2O. Thus, the average force constant of VO_5 structural units increases with increasing V_2O_5 content. The change of density and molar volume with V_2O_5 content reveals that the decrease in density is related to the replacement of high dense PbO with low dense one V_2O_5, where the increase in the molar volume can be attributed to the larger packing factor of V_2O_5 than that of PbO. The sound velocities and Debye temperature show a decreasing trend which is attributed to the increase in the vibrations of the glass network. The observed decrease in the bulk modulus is associated with a decrease in the number of bonds per unit glass formula unit as a direct effect of V_2O_5 on the coordination number of the vanadate and lead structural units.

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