

Structural Analysis of Glassy Lead Borate Containing MoO₃ In Relation to Its Optical Properties

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Glasses with the base un-doped composition 80%PbO.20%B₂O₃ and that containing MoO₃ with 1% and 5% were studied using X-ray diffraction (XRD) technique. The scattered X-ray intensity was Fourier transformed and the Radial Distribution Function (RDF) analysis was applied to extract the structural information's of these samples. The first nearest neighbor is observed at 1.315Å, 1.456Å and 1.499Å respectively for the un-doped and doped samples. This first nearest neighbor seems to be due to B-O correlations in the form of triangles. The second nearest neighbor is centered at about 2.12Å for the base sample and is shifted to 1.92Å for the doped ones; this peak is attributed to O-O correlations having a coordination number of about two. The B-B pairs were located at 2.36Å for the investigated samples with a reduced coordination number, ~2.0. The coordinated Pb-O pairs were observed at 2.60Å with a form of PbO₃ in the sample having 1% MoO₃, and an appreciable change in both Pb-O bond length and coordination number was noted in the other two samples. The Pb-O pairs in the two samples(0.0 and 5% MoO₃) were stretched (at 2.80Å) and arranged in the tetrahedral form(PbO₄). The peak located at 3.55Å for the base sample and that contains 1% MoO₃ is mainly due B-O pairs arranged in BO₄ and BO₃ forms. In the third sample (having 5% MO₃) both of Non-Bridging Oxygen(NBO) and Bridging ones(BO) in the connected B-O pairs are evolved; at 3.24Å and 3.64Å with an arranged BO₃ form. The Pb-Pb metallic correlations were observed at ~4.0Å with a coordination number about 4.0 for all samples. The structure of these glassy networks was modeled and the different bond angles were concerned. The XRD experimental findings were supported by IR, Raman and ESR measurements of the studied samples.

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1. Introduction:

A widespread set of very different borate glasses with optical, magnetic, super-ionic conductivity and other technologically interesting properties are currently produced. The optimization of such properties as a function of composition and other preparation parameters requires a good knowledge of the microscopic glassy structure. For many years, glasses containing transition metal ions have attracted attention because of their potential applications in electrochemical, electronic and electro-optic devices [1]. In recent years molecular dynamics (MD) simulation has been used to investigate the structure and properties of many glasses. Due to inadequate bond angles especially B- \hat{O} -B, the MD technique was not able to reproduce, e.g. the boroxol ring with pair wise type potentials [2]. The presence of high content of lead oxide in lead borate glasses can be considered as a former/modifier in the glassy matrix having basically B_2O_3 as a glassy former. The role of low and high concentrations of MoO_3 in glass has not been received much attention. Therefore, it was thought of interest to study the correlation between the properties of lead borate glasses containing MoO_3 and their network structures and also to gain more information about the state of Mo in such glass system as elucidated by Gohar [3]. Recently, Umesaki et al. [4] have studied $K_2O.B_2O_3$ using pulsed neutron total scattering measurements to reveal the structures of alkali borate glasses by XRD, NMR and Raman spectroscopy. Neutron diffraction technique was also used and revealed an interesting new structural features [4]. The short Range Order (SRO) of glasses in the systems $MnO-B_2O_3$ and $PbO-MnO-B_2O_3$ has been recently discussed by applying XRD by Staneva [5]. In this study only the Metal-Metal pairs (Pb-Pb) or (Mn-Mn) are studied.

Studies in the literature concerning the XRD-structural analysis of the glassy $PbO-B_2O_3-MoO_3$ systems with small contents of MoO_3 (1% & 5%) are limited. The present study is mainly devoted to throw some lights on the structural features of this system and to correlate this structural analysis with the optical properties of these glassy matrix using IR and Raman techniques.

Our work dealt with $80PbO-20B_2O_3$ glass and MoO_3 was introduced with 1% and 5%. X-ray structural analysis was used and the role of MoO_3 will be discussed via the Radial Distribution Function(RDF) analysis. Besides Raman and infra red absorption studies are carried out to reveal the structural groupings with those of structural interest.. A further objective of this work is to follow up the possible states of molybdenum in such lead borate glass by electron spin resonance measurements.

2. Experimental Details

2.1. Preparation of Glasses:

The parent and doped lead borate glasses were prepared using chemically pure materials B_2O_3 was introduced as orthoboric acid (H_3BO_3), and PbO was added as red lead oxide (Pb_3O_4) while MoO_3 was added as such. The thoroughly mixed batches were melted under normal atmospheric condition in platinum crucibles in electrically heated furnace at $1000 \pm 10^\circ C$ for 1 hour. Homogenization was achieved by rotating the melt two times. The melts were cast as required and carefully annealed at about $380^\circ C$ inside a muffle furnace which was left to cool to room temperature at a rate of $20^\circ C/hour$.

2.2. X-ray diffraction analysis:

2.2.1. X-ray experimental set up:

Philips powder diffractometer of X'pert (MPD) system with Bragg-Brentano para focusing of reflection geometry technique and graphite monochromated $Mo-K_\alpha$ radiation ($\lambda=0.709\text{\AA}$) was applied in case of doped samples. A fixed divergence slit of 1° and a receiving slit of a height 0.1 mm were used. Soller slits of 0.04 rad were used in both the incident and diffracted beams. Data were collected over the range $4^\circ \leq 2\theta \leq 116.5^\circ$ in $0.04^\circ 2\theta$ steps with a counting time of 10 seconds. The $Cu-K_\alpha$ radiation ($\lambda=1.5405\text{\AA}$) was applied for un-doped sample with the same previous conditions.

2.2.2. RDF formulation analysis:

The total structure factor of a glass is given as:

$$S(K) = \{I(K) - [\langle f^2 \rangle - \langle f \rangle^2]\} / \langle f \rangle^2 \quad (1)$$

$I(K)$ is being the scattered corrected X-ray intensity of the atomic species constituting the given specimen, f is the atomic scattering factor, $K=4\pi \sin\theta/\lambda$ is being the magnitude of the scattering vector, and the term $[\langle f^2 \rangle - \langle f \rangle^2]$ is known by the Laue- diffraction, This Laue term is of more significance at small angles (2θ), of scattering. $S(K)$ is related to the deviation from the average number density ρ_0 by a sine transform as:

$$S(K) = 4\pi/K \int r [\rho(r) - \rho_0] \sin(Kr) dr \quad [6] \quad (2)$$

where $\rho(r)$ is the atomic density as a function of the radial distance r ,

$$\rho_0 = \rho x N / A x 10^{24} \quad (3)$$

ρ is the sample density in gm/cm³, N is the Avogadro's number, A is being the sample atomic weight and the integration limit is 0- ∞ . RDF is given as:

$$4\pi r^2 \rho(r) = rG(r) + 4\pi r^2 \rho_0 \quad (4)$$

where G(r) is the reduced RDF, so :

$$G(r) = 4\pi r [\rho(r) - \rho_0] = 2/\pi \int K [S(K) - 1] \exp(-\alpha^2 K^2) \sin(Kr) dK \quad (5)$$

then :

$$RDF = 4\pi r^2 \rho(r) = 2r/\pi \int K [S(K) - 1] \exp(-\alpha^2 K^2) \sin(Kr) dK + 4\pi \rho_0 r^2, \quad (6)$$

$4\pi r^2 \rho_0$ is of a symptotic form. α^2 is the disordering parameter of value $\sim 0.01 \text{ \AA}^2$ mainly used to reduce the effect of spurious peaks (or spurious information's) in the high K-range in the measured data.

For only binary systems in terms of partial densities;

$$S_{\alpha\beta}(K) = 4\pi/K \int r [\rho_{\alpha\beta}(r) - \rho_{0\beta}] \sin(Kr) dr \quad [6] \quad (7)$$

Where $\rho_{0\beta} = C_{\beta} \rho_0$, and C_{β} is the concentration of the atomic species β , ∞ in the previous integral can be replaced by K_{\max} , the accessible available maximum value of K corresponding to the experimental requirement of the collected data at $2\theta_{\max}$ for the amorphous system considered.

2.3. Infrared Absorption Measurements

The infrared absorption spectra of the un-doped and doped glasses were measured at room temperature in the range (4000- 100) cm⁻¹ by an infrared spectrophotometer type Jasco (Japan), FT /IR – 300E Spectrometer using the KBr technique. Pieces of the investigated glasses were pulverized as fine particles and then mixed with KBr in the ratio 2: 200, respectively. The mixture was then subjected to a pressure of 5 tons /cm² to produce clear homogeneous discs. The absorption spectra were measured immediately after preparing the desired discs.

2.4. Raman Spectra Measurements

Raman spectra were measured using FTIR-Raman spectrophotometer, type Nicolet, FT-Raman Module (U.S.A.) with a source NdYAG Laser, $\lambda = 1064$ nm covering the range 3700-100 cm⁻¹. The glass samples were examined in the form of fine powder and references samples of two base lead borate glasses and crystalline lead oxide (PbO) and MoO₃ were also measured.

2.5. Electron Spin Resonance Measurements.

Electron spin resonance spectra were recorded at room temperature on an ESR spectrometer (Bruker, XELEM XSYS – E 500, Germany) operating at 9.808 Hz and using 100 KHz field modulation. The magnetic field was scanned from 480 to 6480 Gauss.

3. Results and Discussion:

3.1. X-ray analysis data.

The X-ray scattered intensity versus K for un-doped sample is given in Fig.1 for a comparative way with the doped ones. The careful smoothing of the data will improve the signal to noisy ratio in the K -space, which in turn improves the obtained data in the real space (RDF data). Inspection of Fig.1 indicates that the prepared amorphous systems are well formed in its amorphous phase and having more than one hump. It is obvious also from Fig. 1 that the same humps have no angular shifts for the samples containing MoO_3 , but only in the case of the sample having 5% MoO_3 , the X-ray intensity increases which means an increase in the scattering power of the X-ray with the increase of MoO_3 content. In other words, the increase of MoO_3 percent to the lead borate glass is assumed to increase its ordering especially in its short range order (SRO). For the three samples the first sharper hump is observed at 2 \AA^{-1} , while the second intense hump is located around 3.10 \AA^{-1} followed by a broader hump at $(4.4-6.85) \text{ \AA}^{-1}$. Another extended more broader hump is also observed at $(6.85-13) \text{ \AA}^{-1}$ in the doped samples. The sharpness in the amorphous first two humps would reflect the good connection of atomic pairs, i.e. good ordered atomic pairs in SRO. In the MRO, the degree of order in the atomic pairs will be decreased, which means the presence of less relaxed atomic bonds. The collected raw data were corrected for the background, polarization and absorption factors, then the corrected data were normalized at low and high angle data ranges [6,7].

Fig.2 represents the structure factor $S(K)$ versus K ($K = 4\pi\sin\theta/\lambda$) in the inverted space of the base amorphous lead borate glass with the two doped samples having 1% and 5% MoO_3 respectively. Since the radiation used for the un-doped sample (0.0% MoO_3) was of longer wavelength ($\lambda = 1.541 \text{ \AA}$), so the maximum allowed K was $\sim 7.605 \text{ \AA}^{-1}$, and the peaks in the K -space suffered a large broadening compared to the using of shorter wavelength. Also in the RDF (real- space), peaks will have a large peak- broadening, i.e. the RDF will be of less resolution and less statistical analysis with the use of longer wavelength X-ray source. The benefit of using Cu-radiation of longer wavelength is to reveal the presence of Pb-Pb correlation's [5]. Fig.3. shows the reduced RDF or $G(r)$ versus r for the base lead borate glass with the other two

doped samples. The truncated K_{\max} was 7.605 \AA^{-1} , the value of α^2 chosen was 0.01 \AA^2 , and the value of the number density ρ_0 in terms of the sample component densities (ρ 's) was taken to be 0.0313 At/ \AA^3 , and the K -space data was carefully smoothed. The values of the bond lengths r 's and the coordination numbers n 's for both the SRO and MRO can be given in table 3.1 for the doped and un-doped lead borate glasses.

Intensity(a.u.) versus K for a-PbB(with $\text{MoO}_3=0.0, 0.01, 0.05$) respect.

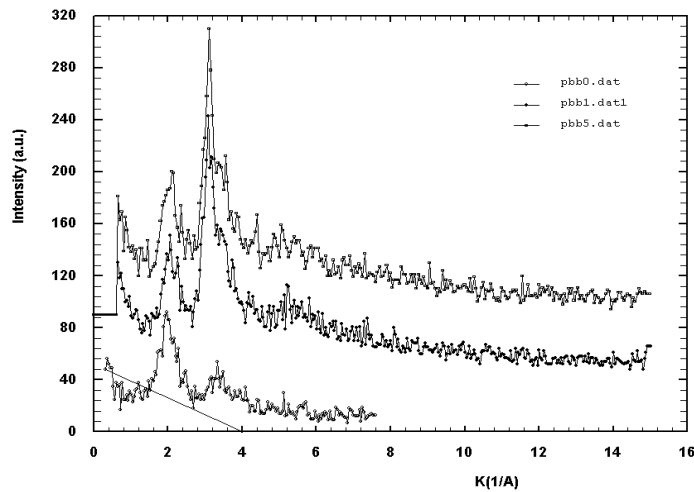


Fig.(1): Intensity of a-PbO-B₂O₃ with 0.0,0.01,0.05 MoO₃respectively against K (in case of 0.0 MoO₃ Cu-radiation is used).

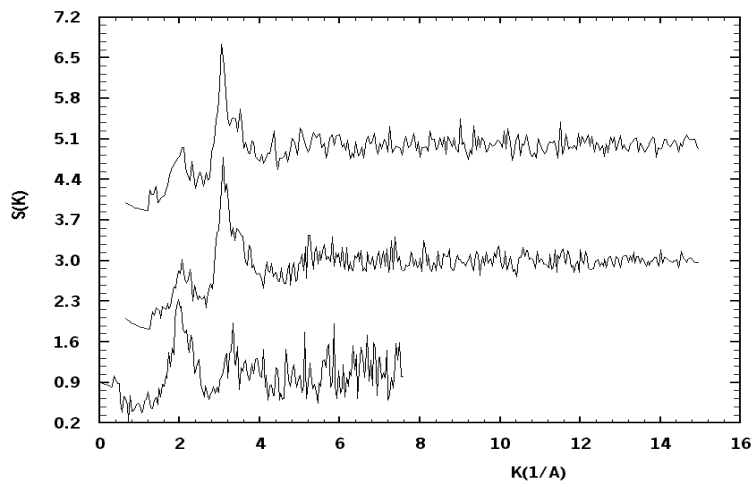


Fig. (2): Structure factor $S(K)$ of a-PbO-B₂O₃ with 0.0,0.01,0.05 of MoO₃ respectively against K .

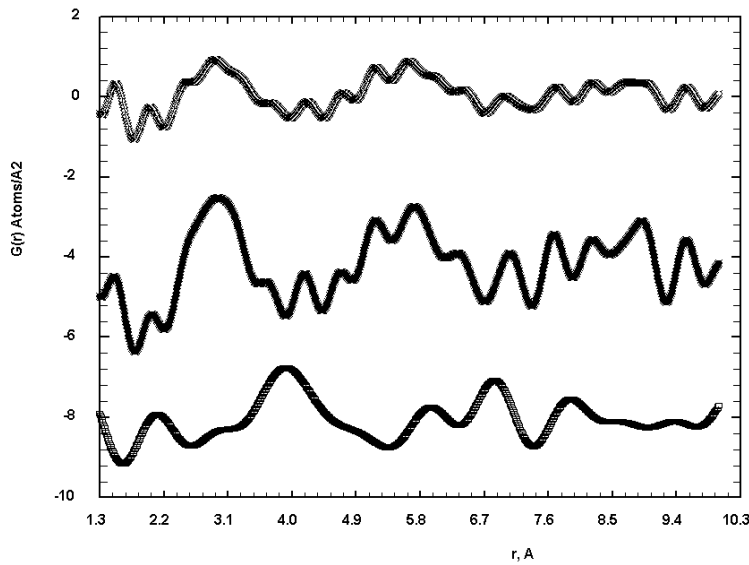


Fig.(3): G(R) as a function of R for a-PbO-B₂O₃ with .0,.01,.05 MoO₃ respectively (for un-doped sample, Cu-source was applied).

Table 3.1 The values of bond lengths, coordination numbers and pair types of SRO and MRO:

Mo O ₃	r ₁ Å	n ₁	r ₂ Å	n ₂	r ₃ Å	n ₃	r ₄ Å	n ₄	r ₅ Å	n ₅	r ₆ Å	n ₆	r ₇ Å	n ₇
0%	1.315	2.45	2.12	1.50	2.80	3.59	3.55	3.92	3.96	4.0				
	B-O		O-O		Pb-O&O-O		B-O		Pb-Pb					
1%	1.456	2.50	1.92	1.50	2.36	1.74	2.60	2.52	3.54	3.0	3.92	3.99		
	B-O		O-O		B-B		Pb-O		B-O		Pb-Pb			
5%	1.499	2.45	1.91	1.50	2.36	1.96	2.81	4.53	3.24	2.82	3.64	2.53	4.09	3.85
	B-O		O-O		B-B		Pb-O&O-O		B-O of (NBO)		B-O of (BO)		Pb-Pb	

* r ± 0.03Å in SRO

** n ± ~ 0.2 in SRO

Table 3.1. and Fig.4 indicate that the first nearest neighbor which belongs to B – O pairs is of trivalent nature (B is surrounded by three oxygen atoms) for all the investigated samples. The centered peak at 2.36Å which is due to B-B pairs in the doped samples had deficient coordination number; about 2.0, instead of 3.0, which may be due to the introduction of MoO₃ in the glass network. The next nearest neighbor which is due to O-O bonds having an elongated bond length (in case of the base sample) and a coordination number of ~1.5. The highly broadened peak observed at ~ 4Å in the base sample has two pre- and post-shoulder located at 2.80 and 3.55Å respectively. The first

shoulder may be due to Pb–O and O–O atomic correlations. The second shoulder located at 3.55\AA is due to B–O bonds (of BO). As it is reported in table. 3.1, the Pb–O pairs are arranged in form of PbO_3 instead of PbO_4 due to the effect of both PbO and MoO_3 as former/modifier systems in the glass network studied [3]. The main peak centered at $\sim 3.95\text{\AA}$ is identified mainly for the Pb–Pb bonds of coordination number about 4.0 in accordance with others as reported by Staneva et al. [5]. As an interesting structural behavior reported in table. 3.1, is the change of BO_4 in the longer r-shells in the base sample to BO_3 in the other doped samples besides to the existence of both BO and NBO in the B–O bonds for the sample containing 5% MoO_3 .

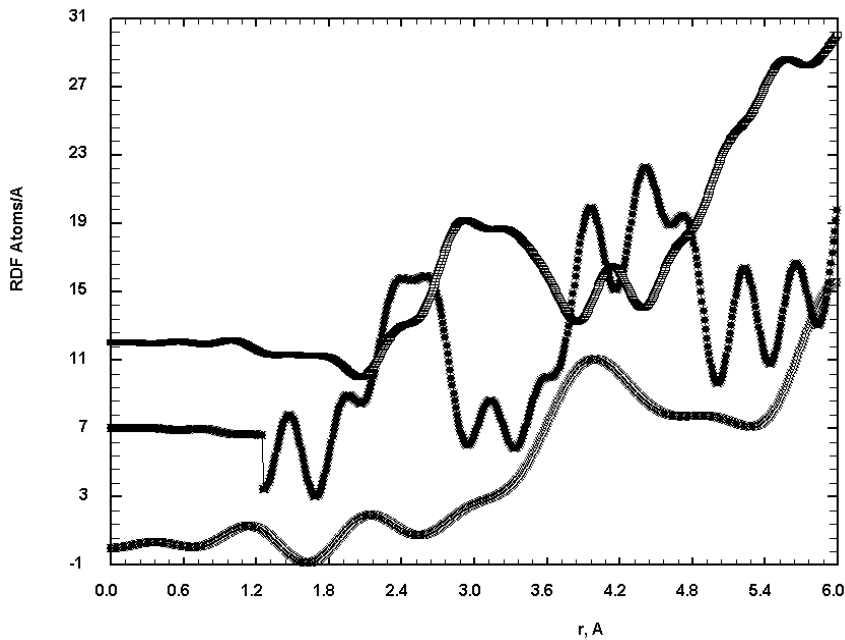


Fig.(4): RDF against R for a-PbO-B₂O₃ with .0,.01,.05 MoO₃ respectively

Our results of a-lead borate with 5% MoO_3 are in more agreement with the results obtained by Wright et al. [7], but with some small deviations in our coordination numbers. With the application of molecular dynamics by Akasaka and Yasui [2], they arrived to results comparable to our RDF structural parameters but some of our bond angles are more relaxed (of smaller values), compared to those obtained in molecular dynamic simulation of the prepared same glasses. Lead borate glasses were investigated also by Hubert et al. [8] using Raman, IR, and EXAFS as spectroscopic methods, and their data are also in good agreement with our results especially in SRO region.

The first coordination shells in the SRO region and the first shell of MRO are simulated. The first nearest neighbor which belongs to B-O bonds is located at 1.499Å and gives a best agreement with the supposed model data of (n, r, σ) , having the values 2.60, 1.50Å, 0.08Å respectively. The formation of both BO_3 and BO_4 groups (may reflect the possibility of dynamic movement of oxygen atoms within this amorphous matrix and this first shell simulations is given in Fig.5. The simulation of the second nearest neighbor gives also an

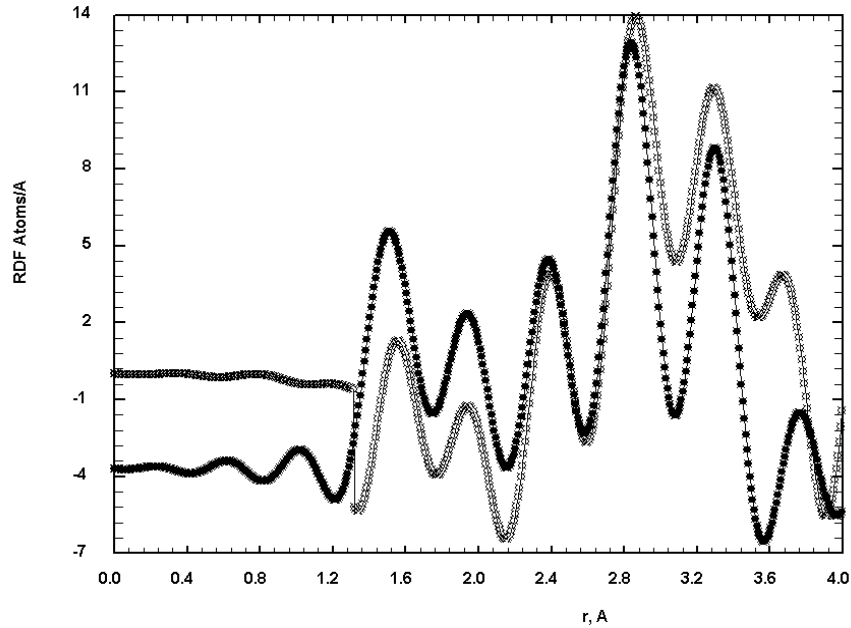


Fig.(5): Simulated RDF with the observed one for the first ordered shells in SRO region.

excellent fit with the experimental data with the values (1.60, 1.92Å, 0.085Å) respectively. These simulated data in the three-dimensional real space clearly indicate that the formation of O-O pairs of two fold coordination, having more or less disordering degree similar to those of B-O pairs. The third nearest neighbor simulation is given and the proposed model having the values of (n, r, σ) as (2.95, 2.64, 0.11Å), which means that the Pb-O bonds are arranged in the form of triangles instead of tetrahedral form, which again points to the atomic deficiency ($n=2.95$) of the correlated Pb-O Pairs. This coordination number deficiency may be interpreted as given before due to the presence of dangling bonds and dynamic movement of oxygen atoms inside the vacant sites of the amorphous matrix of lead borate having 5% MoO_3 content. In other

words the presence of both PbO_4 and PbO_3 would make counterpart in this glass nature as reported by Rabinovich [23] and Fayon et al. [24]. The fourth coordination shell which is attributed to B-O bonds of non-bridging oxygen(NBO) connection is also simulated and the assumed model values of (n,r,σ) are 2.50, 3.27Å , 0.24Å respectively.

3.2. Bond Angle Distribution in Amorphous Lead Borate with 0.0 and 0.05 MoO_3 content:

The different bond angles for lead borate without MoO_3 were: $\text{B}-\hat{\text{O}}-\text{B}=108.278^\circ$ at the SRO peaks, while the $\text{B}-\hat{\text{O}}-\text{B}$ in the MRO is 136.43° , while the $\text{O}-\text{B}-\text{O}$ angle in the MRO is $\sim 78^\circ$. These data of the bond angles agree with those obtained by Akasaka et al. [2]. The bond angle values obtained in the study of a- lead borate with 5% MoO_3 were: $\text{B}-\hat{\text{O}}-\text{B}$ (SRO region)= 103.848° , $\text{O}-\text{B}-\text{O} = 144.68^\circ$ (for MRO), $\text{B}-\hat{\text{O}}-\text{B} = 105.31^\circ$. This clearly indicates that, with the introduction of MoO_3 (5%) in the lead borate matrix the bond angles decreased in the SRO and increased in the MRO, i.e. MoO_3 can be considered as a good glassy former component, causing a high disorder in the MRO, and causes a good ordering in the SRO of a-lead borate matrix. We can suggest that with the high percents of MoO_3 to be introduced in the a-lead borate, some structural modifications may be grown within the glassy matrix which means that MoO_3 will play a modifying role at its high percentages, and plays as a former with its small percentages in the studied a-lead borate glass [3].

3.3. Infrared Absorption Spectra

Table (3.2) depicts the detailed absorption bands and their assignments according to different authors [13-16],[17,18,21,31]. From this information it is obvious the persistence of the absorption band at 700 cm^{-1} which is indicative of the presence of BO_3 or boroxol groups even in the studied glass composition which contains high PbO 80 % and low B_2O_3 20 %. Also the same two mid broad absorption bands which are attributed to the abundance of BO_4 groups ($740\text{-}1120\text{ cm}^{-1}$) and BO_3 groups ($1130\text{-}1520\text{ cm}^{-1}$).

- 5- The small inflection at about 1640 cm^{-1} is ascribed to vibrations of water group together with the broad band extending from $3200\text{-}3640\text{ cm}^{-1}$ which is related to vibrations of hydrogen bonding, molecular water, BOH or hydroxyl groups.
- 6- When PbO is introduced to silicate or borate glasses, there are two ways in which lead ion can get incorporated into the glass [20-22]. PbO may act as a network modifier in the same way as alkali oxide disrupting the bonds connecting neighboring SiO_4 , BO_3 and BO_4 groups. The ionic cross-links provided by lead ions (Pb^{2+}) are stronger than those provided by alkali ions. On the other hand, PbO can be incorporated into the glass as network-

forming Pb-O groups (PbO_4 and/or PbO_3). Additional oxygen for the coordination requirement of lead oxide to form network-formers are naturally provided by alkali or alkaline earth oxide present in the glass or even by a further molecule of lead oxide itself.

- 7- Earlier studies [23,24] on lead borate glasses had indicated that, if the PbO content is low, the Pb^{2+} ions must be considered to behave as modifier and the formation of BO_4 groups proceeds at the rate of two tetrahedral for each added oxygen. Above 15 to 20 mol % PbO, the formation rate of the tetrahedral is reduced, because some of the lead atoms now participate in the network as PbO_4 pyramids, with the Pb atom forming the apex of the pyramid. These pyramids are assumed to preferentially bridge to BO_3 rather than BO_4 units. A noticeable change in the BO_4 units appears at about 30 mol % PbO. This is due to a change in the electron distribution in the B₃-O bonds, which probably results from the replacement of B₃-O-B₄ by B₃-O-Pb bonds. The fractional content of four-coordinated boron (B_4) attains its maximum value of about 0.5 when the PbO and B_2O_3 contents are approximately equimolar. It would seem that the content of the B_4 fraction cannot become higher, because the modified BO_3 units containing one or more B₃-O-Pb bonds are unable to accept a fourth oxygen atom.
- 8- Recent studies [23,24] have postulated that the structure of high lead oxide contains PbO_3 and PbO_4 groups as structural elements but the ratio of them is not clearly established. There are still different views about the coordination number of the lead ions behaving as network formers.
- 9- The effect of the increase in the MoO₃ content is specifically reflected first in the far-infrared spectra (as shown in Table 3.2).

3.4. Raman Spectra

The Raman spectra measured of the MoO-doped glasses, un-doped glasses and reference crystalline PbO and MoO₃ are given in Figures (6-8) and the results can be summarized as follows

- 1- Figure (6) shows the Raman spectra for the lead borate containing 1% & 5% MoO₃. The first glass spectrum reveals a very sharp band at 134cm^{-1} and two medium broad bands with peaks at 900 and 1255cm^{-1} and two other weak peaks at 1927 and 3341cm^{-1} . On increasing the MoO₃ content to 5% glass reveals a spectrum consisting of three prominent and sharp bands at 133 , 305 and 885cm^{-1} and three broad weak bands at 1246 , 1910 and 3311cm^{-1} .
- 2- Figure (7) reveals the Raman spectra for the two un-doped lead borate glasses of the compositions (1) PbO 80% B_2O_3 20% and (2) PbO 90%, B_2O_3 10%. Both the two glasses reveal a very sharp band at 130cm^{-1} in the first glass (80% PbO) and shifts to 139cm^{-1} in the second glass (90% PbO). The

- spectra of the two glasses show additional small broad bands at about 710-711 cm^{-1} , 905 cm^{-1} , 1024 cm^{-1} , 1239 and 1308 cm^{-1} .
- 3- Figure (8) illustrates the Raman spectra for two crystalline references, namely lead oxide (litharge PbO) and molybdenum trioxide MoO_3 . The Raman spectrum of lead oxide (PbO) reveals characteristic two very sharp bands at 144 and 296 cm^{-1} together with very small peaks at 386 and 757 cm^{-1} . The Raman spectrum of molybdenum trioxide (MoO_3) reveal very small peaks at 282, 820 and 993 cm^{-1} .
 - 4- The interpretation of the Raman spectra obtained can be rationalized on the following basis:
 - a) Borate glasses provide an ideal case in comparison to other glass forming systems, to demonstrate the effectiveness of Raman and infrared spectroscopy in glass science [28]. First, boron has the smallest mass compared to other network forming elements and thus the main vibrational modes associated with the glass network appear well above 500 cm^{-1} in the mid infrared. These network modes are well separated from the metal ion site vibrational modes active in the far infrared region, i.e., below $\sim 600 \text{cm}^{-1}$. Second, borate have a rich chemistry because of the ability of boron to change its coordination with oxygen between three and four and this provide a range of anionic environments that can coordinate the modifying metal ions.
 - b) The Raman spectra reveal the appearance of a sharp band at 133-134 cm^{-1} in the two Mo-containing lead borate glasses which is also apparent in the two un-doped lead borate glasses at 130-139 cm^{-1} and is comparable with the sharp band observed in crystalline PbO at 144 cm^{-1} . This suggests the presence of Pb^{2+} in the studied high lead borate glasses as PbO_4 groups.
 - c) The sharp band observed at 305 cm^{-1} in the Raman spectrum of lead borate glass containing 5% MoO_3 is not observed in the two un-doped lead borate glasses but crystalline lead oxide reveals a sharp Raman band at 296 cm^{-1} while crystalline molybdenum trioxide MoO_3 shows a small Raman peak at 282 cm^{-1} . It can be postulated that this Raman band at 305 cm^{-1} can be originated from different site of Pb^{2+} as suggested by Kamitsos et al [29]. Another postulation is that this band can originate from Mo-O-Pb vibration. The exact origin necessitates further work.
 - d) The weak broad bands observed 900 and 1240-1255 cm^{-1} in lead borate glasses containing 1% & 5% MoO_3 can be correlated with borate network of ortho-, penta-, and pyro-borate [8,30].
 - e) The sharp Raman band observed at 885 cm^{-1} in the lead borate glass containing 5% MoO_3 can be assigned to the combined effect of both stretching mode of isolated ortho molybdate (MoO_4)²⁻ groups as observed by Mogus-Milankovic et al [31] and to various $[\text{BO}_4]^-$ containing groups as suggested by Efimov [32].

- f) The weak broad Raman band observed in both the two MoO₃-lead borate glasses at 3311-3341 cm⁻¹ seems to be correlated with molecular water as evidenced by the work of Husung and Doremus[33].

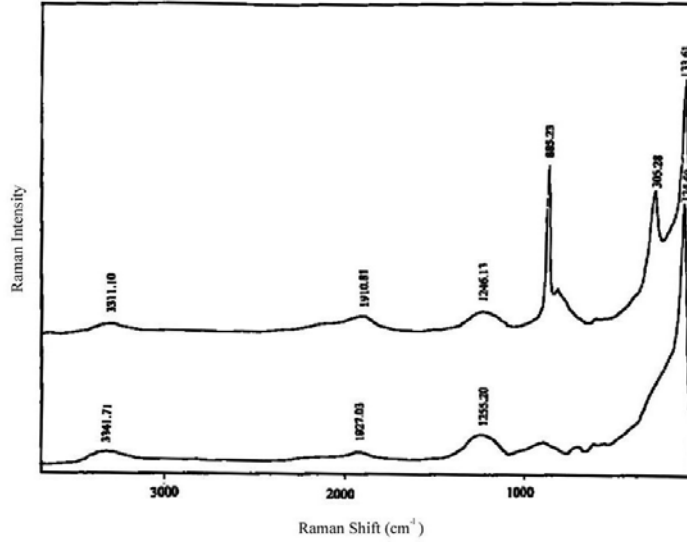


Fig. (6): Raman spectra of lead borate glasses containing 1% and 5% MoO₃.

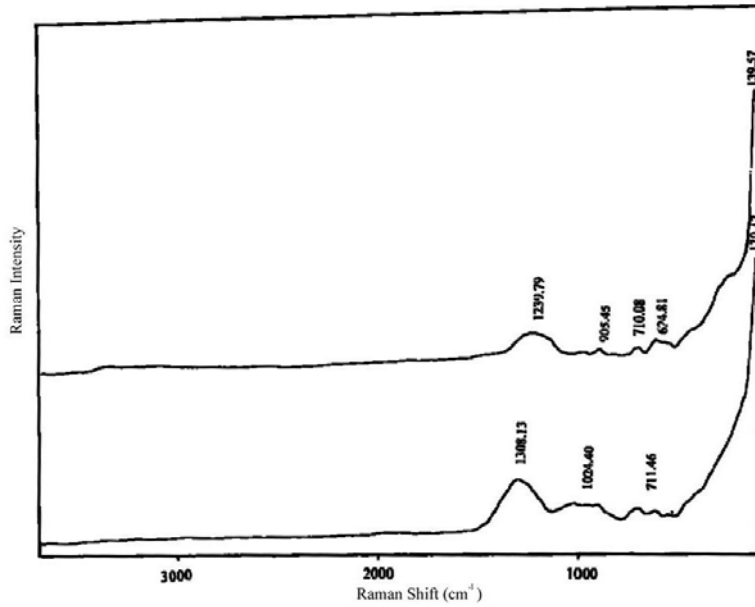


Fig. (7): Raman spectra of un-doped lead borate glasses

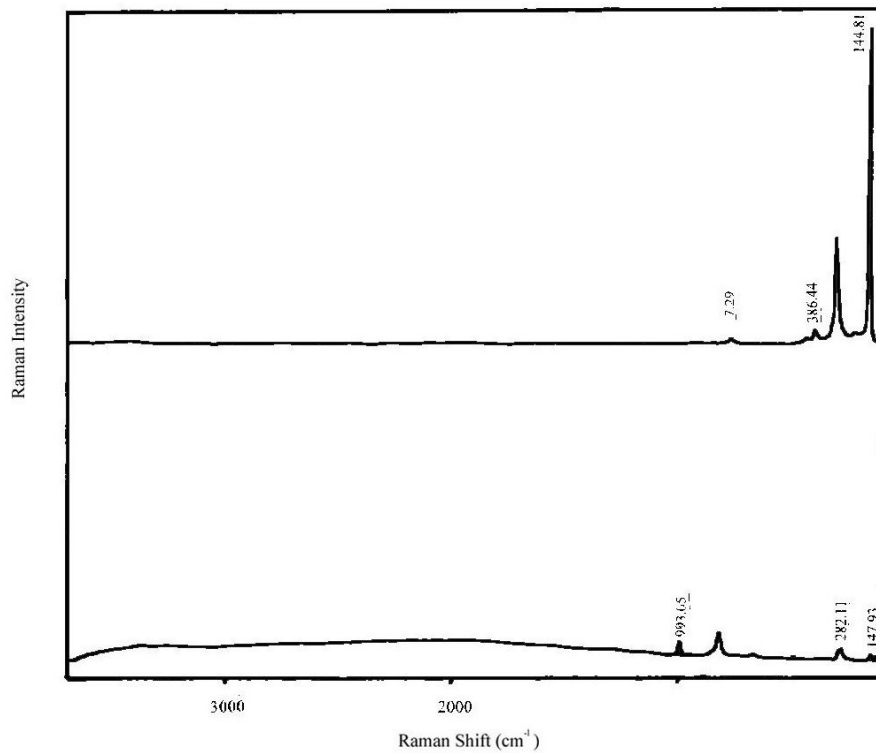


Fig. (8): Raman spectra of crystalline references
(a) PbO (b) MoO₃.

3.5 Electron Spin Resonance data

Figure(9) illustrates the e.s.r spectra of the MoO₃-doped glasses containing 1% and 5% MoO₃ content. Inspection of the figure indicates that the positions of the signals are different with the MoO₃ content. The results indicate first that the species measured are unpaired because e.s.r is sensitive only to unpaired electrons. Also the result indicates that the change in the e.s.r spectra with MoO₃ content may be correlated with the possible change in symmetry or change in the valence. Simon and Nicula [34] have attributed the change in the e.s.r spectra of MoO₃ content in alkali borate glasses to the change of Mo⁵⁺ ions from hexagonal symmetry to rhombic symmetry. Also they assumed that in rich alkali borate glasses, the Mo⁵⁺ is not the main valence. It has been established [35,36] that in silicate and borate glasses, only pentavalent molybdenum ions were obtained, but in phosphate glasses the trivalent molybdenum ions could be stabilized.

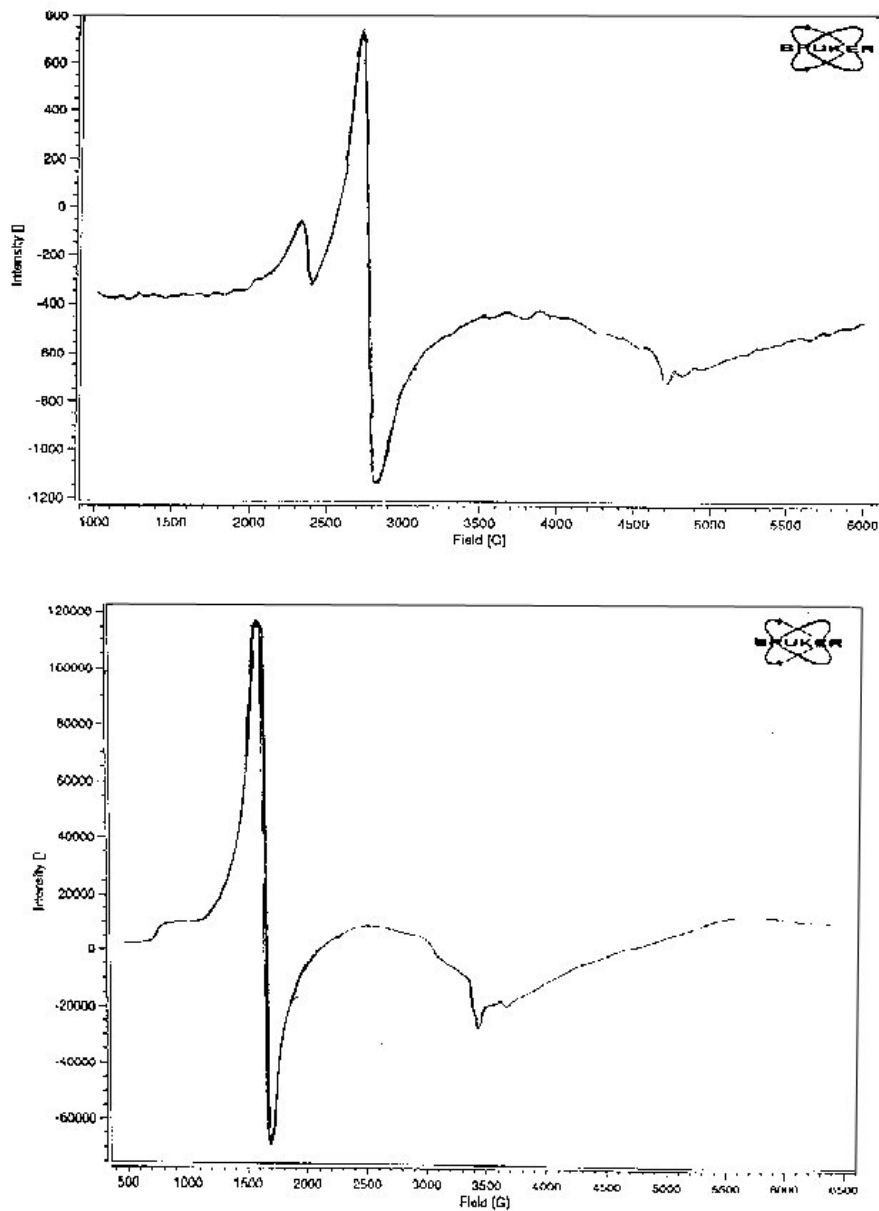


Fig. (9): Electron spin resonance spectra of MoO₃ doped lead borate Glasses (a) 1% MoO₃ (b) 5% MoO₃
(a) PbO 80%, B₂O₃ 20% (b) PbO 90%, B₂O₃ 10%.

In a recent study by one of the authors [37], it was possible to introduce high concentration of MoO₃ (up to 50-70 gm/100 gm glass) in high alkali borate glasses and this seems to stabilize the Mo⁵⁺ valence and gives a similar e.s.r spectra for different concentration of MoO₃. It is believed that in the studied high lead borate glass, molybdenum exhibits in minor ratios as Mo⁴⁺ and Mo³⁺ as it is obvious in the data in Figure (9) which reveal e.s.r. data different from that obtained in alkali borate glasses [37].

Table (4): Infrared absorption bands and their assignment.

Peak position (cm ⁻¹)	Assignment	References
Borate chains		
a- BO₃ groups		
1420-1550	Penta-, meta and pyro-borate units	13,14,17
1350-1400	B-O vibration of various borate rings	
1240-1350	Boroxol rings, tri-,tetra- and pentaborate groups	13,14,17
1190-1240	Boroxol rings, penta-and ortho-borate	
b- BO₄ groups		
1050	Tri-, tetra-, and penta-borate groups	16,17,21,28,31
900-1000	Diborate groups	
720-770	Oxygen bridges between one tetrahedral and one trigonal boron atom	
690-720	Oxygen bridges between two trigonal atoms	
550-630	Bending vibrations of various borate and isolated BO ₃ ³⁻	
Molybdate Groups		
270-307	[MoO ₄] ²⁻	15,18
400-490	[MoO ₆] ⁶⁻ - [MoO ₃] ⁻	
579	Mo-O-Mo	
630-640	Condensed molybdate such as [MoO ₄] ²⁻ and [Mo ₂ O ₇] ²⁻	
681	[MoO ₆] ⁶⁻	
780-880	Stretching vibrations of [MoO ₄] ²⁻ anions	
920-980	Mo-O stretching frequency of [MoO ₆] ⁶⁻	
Lead ions		
400-500	Covalent Pb-O	15,18
290-300	Ionic Pb-O bonds	
100-200		

Conclusions:

1. X-ray analysis did not reveal a significant role for 1% MoO₃ in the lead borate glass, but for 5% MoO₃ content, some structural changes could be involved in the structural information obtained such as: the bond length r , the coordination number n , and the degree of disordering in the amorphous matrix σ . Also the bond angles of both B- \hat{O} -B and O-B-O would be changed by the introduction of this percent of MoO₃.
2. The structural units BO₃ are presented with B-O linked pairs with NBO and BO for a-lead borate (with 5% MoO₃) in the MRO and in the SRO the B-O pairs are arranged in form of triangles. The coordination number of B (O) pairs may suffer a deficiency due to the formation of some dangling bonds inside the glassy matrix, and a dynamic movement of oxygen atoms from SRO to MRO in the amorphous system.
3. The Pb-O pairs are indicated to exist in the form of both PbO₃(as our model predicted), and also in form of PbO₄ tetrahedral, the ratio of one form to the other (PbO₃/PbO₄) is not exactly determined. The RDF analysis revealed Pb-Pb correlation's using the two radiations (Cu-source and Mo-source), beside the detection of B-B pairs in SRO.
4. The IR, Raman and ESR measurements gave a good correlation and are of complementary nature to those information obtained from X-ray analysis, i.e. the trend of the measured properties of the samples can be interpreted from the information obtained from X-ray structural analysis.
5. The studied high lead borate glasses give data indicating a good former tendency of B₂O₃, a partial former/modifier of PbO. The increasing ratio of MoO₃ show the tendency for playing a modifying role in the glass matrix of lead borate glasses.
6. More confirmation tools are needed to avoid the considerable controversy of the presence of Pb-Pb pairs at around 4Å as may be given in our G(R) results (using X-ray of $\lambda=1.541\text{\AA}$) in the investigation of base lead borate (80% PbO-20% B₂O₃) [5,7]. This Key of study may open new roots of studying this high lead borate glasses with increased MoO₃ ratios.
7. The identification of Mo-O bonds is not revealed in this X-ray study (it may be formed in the form of MoO₄ at $r\sim 3.65\text{\AA}$), as suggested by IR and Raman studies.

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