Unusual visible absorption
in high PbO lead borate glass

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A series of glasses in the system xPbO·$(100 - x)$B$_2$O$_3$ (x = 45, 55, 65 mol %) were prepared using analytical grade PbO consisting of a mixture of orthorhombic and tetragonal phases (ca. 1:1, w/w) and H$_3$BO$_3$ melted in silica beaker in the temperature range of 575–900 ºC for 30 min under normal atmosphere. Only the 55PbO·45B$_2$O$_3$ glass prepared at 575 (L2), 650 (L3) and 700 ºC (L4) showed several optical absorption bands in the visible region. However, all the bands disappeared either when a 1.7 mol % equivalent PbO from Pb$_3$O$_4$ was added in the batch or the melting temperature was increased to more than 800 ºC. L2 glass showed a broad absorption band at ca. 485 nm which was thought to be due to combined effect of nanometallic lead (Pb^0) and Pb$^+$. The formation of hexagonal nano-Pb^0 particles of 7–13 nm size in 55PbO·45B$_2$O$_3$ glass melted at 575–700 ºC was confirmed by TEM and Pb$^+$ was identified by a broad EPR signal with g-value at ca. 2.00. Optical absorption at ca. 485 nm and 565 nm (broad shoulder) was observed in L3 glass whereas a new peak at ca. 525 nm appeared in L4 which was identified due to Pb^{3+} by EPR signal with g-value ca. 2.176 and **A**-tensor, ca. 6340×10^{-4} cm^{-1}. A mechanism for the formation of Pb^0, Pb$^+$ and Pb^{3+} has been proposed.

Key words: *lead borate glass; nanometallic lead; microstructure; EPR; visible absorption*

1. Introduction

Lead borate glasses possess an enhanced optical non-linearity due to high polarizability [1, 2] of Pb^{2+} ions in glass matrices. They are attractive materials [2] for applications in waveguides, all optical switches, stimulated Raman amplifiers etc. Metallic lead particles [3] of nanometer dimensions have been found in silica glasses implanted with Pb$^+$. Such glasses have non-linear optical properties which make them possible candidates for optical switching devices [3]. Reduced lead silicate glasses [4] having three different valence states of lead, i.e Pb^0, Pb$^+$ and Pb^{2+} are used as continuous strip dynode materials in electron multipliers. Although lead borate glasses par-

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ticularly with high lead content have low glass transformation temperature and characteristic light yellow colour due to a tail of Pb^{2+} ion absorption [5] in the UV-region, they are highly transparent [2] in the visible and NIR regions. On exposure to high-energy particles, lead containing glasses exhibit optical absorption [6, 7] in the ultraviolet, visible and NIR regions due to trapping of holes and electrons in the vicinity of Pb^{2+} ions.

In preparation of lead borate glasses, Pb_3O_4 is the main source of PbO but sometimes lead monooxide (PbO) is also used. Extensive studies [1, 2, 5, 6, 8–12] have been carried out on the optical properties of the glasses which have been prepared at and above 800 ºC but no data have been found on the glasses melted at low temperature (below 800 ºC). On the other hand, optical properties of the low-melting lead borate glasses prepared from PbO of orthorhombic (o-PbO) and tetragonal (t-PbO) mixtures are also not available in the literature. Therefore, in the present work high PbO containing lead borate glasses were prepared in the range of 575–900 ºC using analytical grade lead(II) oxide (PbO) (consisting of o-PbO and t-PbO mixture, ca. 1:1, w/w) and boric acid and characterized by UV-VIS spectra, electron paramagnetic resonance spectrometry and transmission electron microscopy to find out visible absorption behaviours.

2. Experimental

A series of glasses (Table 1) in 50 g quantity were prepared in the system, xPbO·$(100 - x)$B$_2$O$_3$ (x = 45, 55, 65 mol %) using analytical grade lead(II) oxide

Table 1. Compositions and characteristics of lead–borate glasses

Glass No.	Batch composition [mol %]		Melting temperature [ºC]	Annealing temperature [ºC]	Colour	Density [g·cm^{-3}]	UV cut off wavelength, λ_{50} [nm]
	PbO	B$_2$O$_3$					
L1	45	55	770	400	light yellow	5·55	347.4
L2	55	45	575	340	pink	6.25	385.5
L3	55	45	650	340	pink	6.22	385.0
L4	55	45	700	340	pink	6.21	382.8
L5	55	45	800	340	light yellow	6.09	374.9
L6	55	45	900	340	light yellow	5.87	366.2
L7	55[a]	45	650	340	light yellow	6.20	382.5
L8	65	35	620	320	light yellow	6.46	390.1

[a]1.7 mol % equivalent PbO from Pb_3O_4 and the rest from lead(II) oxide yellow.

yellow (PbO, puriss., ≥ 99.0%, Fluka, Switzerland), red lead (Pb_3O_4, 99.0%, Aldrich, Wisconsin) and boric acid (H_3BO_3, puriss., ≥ 99.5%, Fluka, Switzerland) and melted in the temperature range 575–900 ºC for 30 min under normal atmosphere in silica beaker (150 ml capacity, Infusil, India) with stirring by silica glass rod. The melt was poured onto preheated mild steel mould and annealed at 320–400 ºC for 1 h depending upon composition. The glasses were cut with diamond cutting tool, ground and polished into rectangular plates. Density of polished glass samples ($25 \times 15 \times 10$ mm^3) were measured following Archimedes principle using xylene as an immersion fluid. UV-VIS absorption and transmission spectra of the polished glass samples ($25 \times 15 \times 1$ mm^3) were measured using Perkin Elmer spectrophotometer (Lambda 20, wavelength accuracy: ±0.3 nm; photometric accuracy: abs. ±0.003, < 0.02 % T) and X-band electron paramagnetic resonance (EPR) spectra of powder glass samples were recorded by using Varian Spectrometer (model, E109) with 100 kHz field modulation and 9.500–9.515 GHz microwave frequency region at room temperature. Microstructure of the powdered glass samples was evaluated by transmission electron microscopy (TEM, JEOL, JEM-200CX).

3. Results and discussion

The absorption spectra of the glasses (L1–L8) are shown in Fig. 1. The spectral behaviour of the glasses with the same composition ($55PbO \cdot 45B_2O_3$) and annealing time (1 h) differs with changing of the melting temperature. A broad absorption band, peaking at ca. 485 nm appeared (curve L2) for the glass sample melted at 575 ºC. The
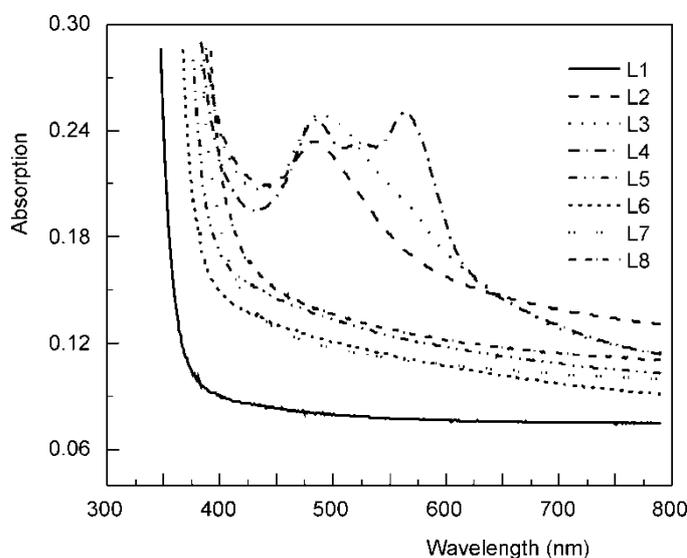

Fig. 1. UV-VIS absorption spectra of glasses (1.0 mm thick).
L1–L8 symbols indicate the glass numbers as given in Table 1

intensity of this band increased with a broad shoulder at ca. 565 nm (curve L3) when melted at 650 ℃. It is very interesting to note that when melted at 700 ℃, the spectral behaviour dramatically changed and three distinct peaks (curve L4) appeared at ca. 485 nm, ca. 525 nm and ca. 565 nm. All the glasses having the same composition (55PbO·45B$_2$O$_3$) and melted in the temperature range 575–700 ℃ were light pink in colour, and the colour disappeared when the melting temperature was increased over 800 ℃ showing no absorption peaks in the visible region (curves L5 and L6). Further, it was also observed that the light pink colour as well as absorption peaks of the glass samples also disappeared (curve L7) when 1.7 mol % equivalent PbO was introduced in the same glass composition (L7) from Pb$_3$O$_4$ and melted at 650 ℃ for 30 min. No absorption peaks (curves L1 and L8) appeared for the glasses having the compositions, 45PbO·55 B$_2$O$_3$ and 65PbO·35 B$_2$O$_3$.

To show the effect of melting temperature on the UV cut off wavelength ($\lambda_{50,}$ arbitrarily defined as the wavelength at which the transmission rises to 50.00%) which is associated [13] with the excitation of electrons of oxygen anions in the glass, the λ_{50} was determined from transmission spectra (Fig. 2) and has been shown in Table 1. The
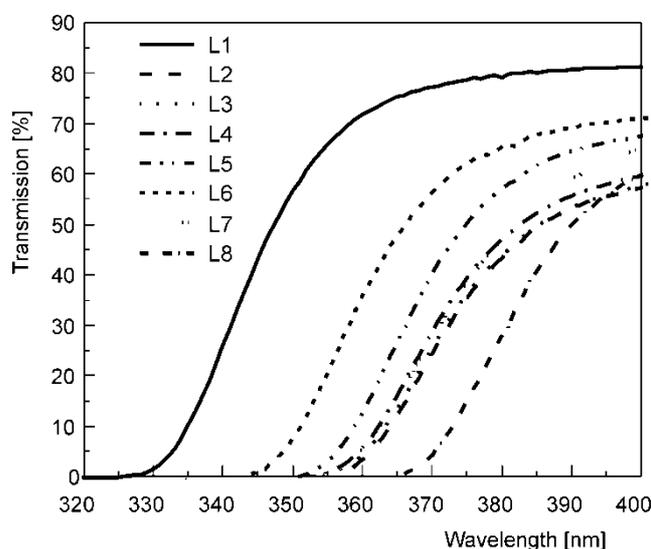

Fig. 2. Transmission spectra of glasses (1.0 mm thick) showing UV cut off wavelengths.
L1–L8 symbols indicate the glass numbers as given in Table 1

shifting of λ_{50} towards higher wavelength region [13] indicates the increase in concentration of non-bridging oxygen (NBOs) in the glass. It is also known [13] that with increasing concentration of PbO, λ_{50} shifts towards longer wavelengths. In L1 (45PbO·55B$_2$O$_3$) glass λ_{50} appeared at 347.4 nm (curve L1) which shifted to 390.1 nm (curve L8) in L8 (65PbO·35B$_2$O$_3$) in line with the above principle. In the case of 55PbO·45B$_2$O$_3$ glasses prepared in the temperature range of 575–900 ℃, it is seen (Table 1) that with increasing melting temperature from 575° to 700 ℃, there is a little

shifting of λ_{50} (2.7 nm) and change of density (0.04 g·cm^{-3}) indicating the minor composition change during this melting temperature range due to little loss of PbO by evaporation [14]. However, unless there had been evaporation of B$_2$O$_3$ from the melt it would have shown an increase in density [13]. But at or above 800 ℃ melting temperature, λ_{50} shifted little more (> 8 nm) towards shorter wavelengths indicating more loss of PbO from the glass melt.

Sometimes in high lead glasses the formation of metallic lead particles has been observed [15] during glass melting due to reduction caused by the unavailability of oxygen. If the same phenomenon is presumed in the present study, then the introduction of an additional source of oxygen could prevent the reduction problem. Therefore, addition of 1.7 mol % equivalent PbO from analytical grade Pb$_3$O$_4$, an additional source of oxygen, resulted in a light yellow coloured glass when melted at 650 ℃ temperature. This indicates that addition of Pb$_3$O$_4$ supplies the available oxygen to the glass network by the following decomposition reaction [16] (Eq. (1)) and prevents the reduction reaction:

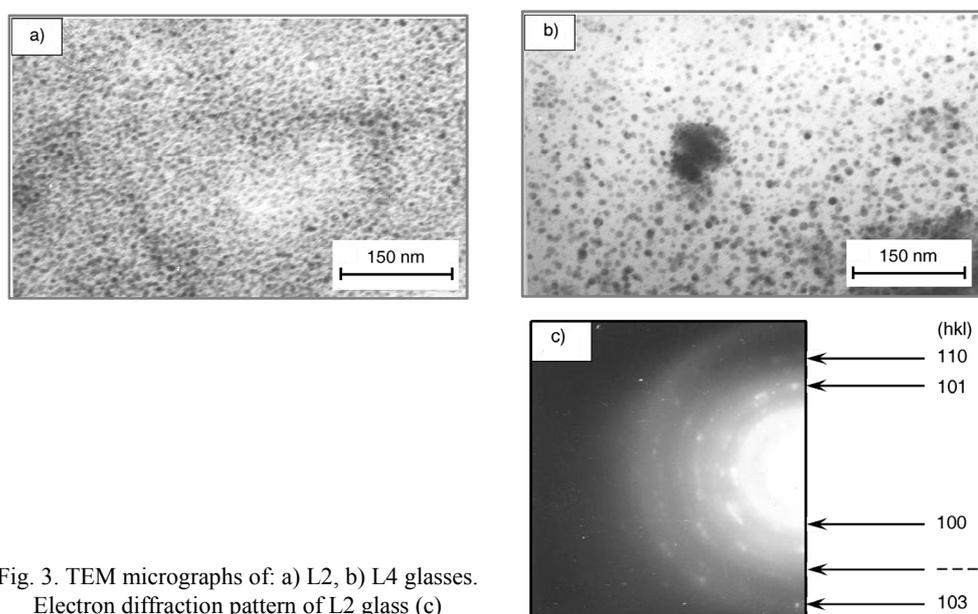$$2Pb_3O_4 = 6PbO + O_2 \qquad (1)$$

Fig. 3. TEM micrographs of: a) L2, b) L4 glasses.
Electron diffraction pattern of L2 glass (c)

To confirm the above assumption and the presence of metallic lead particles formed in the 55PbO·45B$_2$O$_3$ glasses during melting in the temperature range from 575 ℃ to 700 ℃, a transmission electron microscopic (TEM) study was done. It was observed that only the pink coloured glass samples showed the presence of nanometallic lead particles. The microstructure (Fig. 3a) of L2 glass shows nanoparticles (black dot) in the range of 7–11 nm. With increasing melting temperature to 700 ℃

(L4 glass), the particle size (Fig. 3b) slightly increases (8–13 nm). It was seen that electron diffraction patterns of these samples are identical (Fig. 3c) and support the presence of metallic lead particles with hexagonal crystal structure [17]. No evidences of the presence of nano-lead particles were observed in L5 and L7 glasses.

The reduction of Pb^{2+} to Pb^0 in lead glasses can be explained if we consider the asymmetric electron density distribution due to strong polarizability of Pb^{2+} ions [18]. In lead glasses, Pb^{2+} ions may be similar to Pb^{4+} ions in one direction and metallic lead atom in the other which can be considered as an internal redox reaction [18] as given in Eq. (2).

$$Pb^{2+} \rightleftharpoons \frac{1}{2} Pb^{4+} + \frac{1}{2} Pb^0 \qquad (2)$$
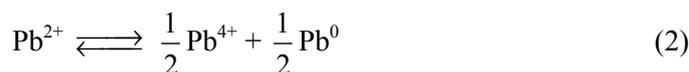
It might be possible in Eq. (2) that the effect of increasing oxygen concentration favours backward reaction and vice versa. In this way, it is believed that when oxygen availability is lower, the system favours the forward reaction as shown in Eq. 2.

The optical absorptions at ca. 485 nm of lead–borate glass prepared at 575 ºC may be thought of due to presence of nanometallic lead particles which is commonly referred to as surface plasmon resonance (SPR). However, the optical absorption [19] which is dependent on the size and electronic structure of lead particles appeared in the UV region. Hence, the absorption at ca. 485 nm may not be solely due to nanometallic lead particles. It can be presumed that formation of metallic lead particles reduces its adjacent higher valent lead ions i.e. Pb^{2+} and Pb^{4+} present in the glass and forms lower valent ions as proposed in the following equations:

$$Pb^{2+} + Pb^0 = 2Pb^+ \qquad (3)$$

$$Pb^{4+} + Pb^0 = Pb^{3+} + Pb^+ \qquad (4)$$

From the above two equations, the formation of both Pb^+ and Pb^{3+} ions is probable in the lead borate glass in presence of metallic lead particles. Barker et al. [7] showed that two bands appear at ca. 375 nm and ca. 525 nm in γ-rays irradiated high lead-silicate glasses, and it seems reasonable to associate them with Pb^{3+} in network-modifying PbO_4 units. In irradiated lead-doped fluoride glasses, absorption band observed [7] at ca. 404 nm in the visible region has been identified as Pb^+ ion formation. Therefore, the optical absorption at ca. 485 nm for the glasses melted within the range of 575–650 ºC is not purely either due to nano-Pb^0 particle or Pb^+ alone, formed according to the Eqs. (3) and (4) but might be responsible due to combined effect of both. Again, with increasing melting temperature to 700 ºC one distinct peak appeared at ca. 525 nm which could be responsible [7] for Pb^{3+} ions.

Since all the species, Pb^0, Pb^+ and Pb^{3+} are paramagnetic [3] due to presence of conduction electrons, p-electrons ($6s^2 6p^1$) and s-electrons ($6s^1$), respectively, it is imperative that electron paramagnetic resonance (EPR) study could be able to explain their existence in the glasses. EPR of all the glass samples were done and it was observed that only the pink coloured samples (L2, L3 and L4) were found paramagnetic

(Fig. 4). L2 and L3 glass samples showed a very broad resonance signal (curves L2 and L3) with $g \approx 2.0$ indicating the presence of Pb^+ ion [3] which supported the above reactions (Eqs. (3), (4)). The sample L4 showed a prominent broad EPR signal (curve L4) with $g \approx 2.176$ and gave a large **A**-tensor, ca. 6340×10^{-4} cm^{-1} indicating that the resonance was due to unpaired 6s electrons [20] of Pb^{3+} ions with non-magnetic nuclei (maximum abundance) [21] showing absorption at ca. 525 nm [7] in the visible region (curve L4, Fig. 1). The large positive *g*-value shift of Pb^{3+} ions might have been caused by the covalency [20] of Pb–O bond. The presence of Pb^+ ions could be a reason for the anisotropic nature of EPR signal observed in L4 glass sample. There is no characteristic EPR signal of Pb^0 ions observed in L2 to L4 glasses, which might have overlapped due to the spectral broadening of EPR signal of Pb^+. The absorption peak at 565 nm (curves L3 and L4, Fig. 1) could not be identified as any extra EPR signal was found for its appearance.
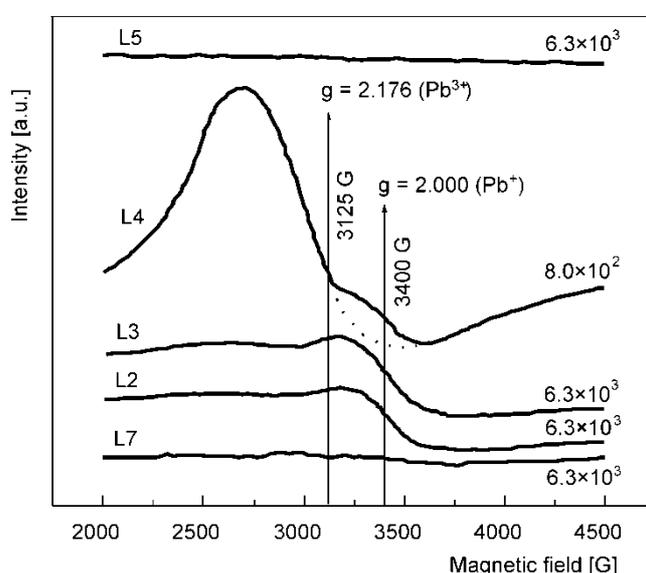

Fig. 4. Room temperature EPR spectra of L2–L5 and L7 glasses
(receiver gain is given inside the figure at the right hand side)

Oxygen diffusion [22] from the ambient atmosphere into the glass melt is possible and the rate of oxygen diffusion depends upon the viscosity of the glass melt which in turn depends on the melting temperature. Thus, with increasing melting temperature, viscosity of the glass melts decreases, which enhances the rate of oxygen diffusion at the higher melting temperatures. Therefore, disappearance of absorption peaks at ≥ 800 °C might be due to dissolution [19] of elemental lead cluster and subsequent oxidation of Pb^0 and Pb^+ to Pb^{2+} (the normal oxidation state of lead) and Pb^{3+} to Pb^{4+}. The reason for the peculiar visible absorptions restricted only to $55PbO \cdot 45B_2O_3$ glass composition is yet to be explored and further research work is required for its explanation.

4. Conclusion

Lead borate glass, $55PbO \cdot 45B_2O_3$ (mol %) melted at 575–700 ºC in air using PbO consisting of tetragonal and orthorhombic mixture, exhibits several unusual visible absorption bands originating from hexagonal nanometallic lead particles together with aliovalent lead ions.

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