J Mater Sci (2009) 44:3061–3071
DOI 10.1007/s10853-009-3406-y

Interactions of gamma rays with tungsten-doped lead phosphate glasses

Fatma Hatem ElBatal · Samir Yousef Marzouk

Received: 24 December 2008 / Accepted: 16 March 2009 / Published online: 3 April 2009

Abstract Undoped lead phosphate glass of the composition PbO 50 mol%, P_2O_5 50 mol% together with samples of the same ratio doped with various WO_3 contents were prepared. UV–Visible spectroscopic studies were measured out in the range 200–1100 nm before and after successive gamma irradiation. Infrared and Raman spectroscopic measurements were carried out for the undoped and WO_3-doped samples. All the prepared samples are observed to absorb strongly in the UV region due to the combined contributions of absorption from trace iron impurities and sharing of lead Pb^{2+} ions. The bluish WO_3-doped lead phosphate samples reveal visible absorption bands which are attributed to the existence of pentavalent W^{5+} ions. ESR measurements support this assumption. Infrared and Raman spectra indicate the presence of metaphosphate chains as the structural main building units and the possible presence of appreciable pentavalent ($W^{5+}O_3$) of W^{5+} units together with hexavalent WO_4 units. Gamma irradiation reveal the shielding behaviour of the studied tungsten-doped lead phosphate glasses due to the combined presence of heavy Pb^{2+} ions and tungsten ions.

Introduction

Tungsten oxide, WO_3, like molybdenum oxide, MoO_3 can be added to glasses with high PbO contents to manufacture vitreous colours or enamels [1]. WO_3, even in excess of 3% by weight, is known to give no visible colouration to sodium silicate or sodium borate glasses melted under oxidizing conditions [2]. Although tungsten can exhibit six different oxidation states, 0, +2, +3, +4, +5 and +6 in its compounds [3], yet in glasses, tungsten is accepted [4–11] to be found as trivalent W^{3+}, tetravalent W^{4+}, pentavalent W^{5+} or as hexavalent W^{6+} or combination of some of them. The ability of tungsten to have several oxidation states opens possibilities for electro-optical applications especially with phosphate glasses [4, 6, 10]. The presence of W^{5+} ions imparts to phosphate glasses bluish colours that change with composition [12]. It is evident that the fraction of W^{5+} ions imparting the bluish colour decreases as the alkali oxide in phosphate glasses increases [12, 13]. Further study is needed to justify and confirm the exact nature of bluish tungsten W^{5+} ions in glass and particularly in phosphate one.

It is accepted that when subjected to ionizing irradiation (e.g. gamma rays, UV rays, etc.), most glasses acquire radiation-induced defects which may give rise to optical and/or ESR absorption bands. Owing to the non-periodic nature of the glass structure, the radiation-induced absorption in glass generally consists of overlapping absorption bands rather than discrete bands as formed in ionic crystals. The principal effect of ionizing gamma irradiation results from almost purely electronic processes [11, 13]. Specifically, these effects occur because electrons are excited to leave their normal positions and move or travel through the glass network. In particular, the addition or the removal of one or more electrons from intrinsic

F. H. ElBatal (✉)
Glass Research Department, National Research Center, Dokki, Cairo, Egypt
e-mail: fh_elbatal@yahoo.co.uk

S. Y. Marzouk
Electron Microscope and Thin Film Department, National Research Center, Dokki, Cairo, Egypt

defects or impurity centers results in the formation of induced colour centres which can absorb light. Some of the radiation damage processes involve photochemical reaction especially for the transition metal ions. However, some glasses containing heavy metal ions or transition metal tons exhibit shielding behaviour towards successive gamma irradiation [11, 13].

This study aims to conduct UV−Visible, infrared, Raman and electron spin resonance spectroscopic studies of some lead phosphate glasses of the basic composition (PbO 50 mol%, P_2O_5 50 mol% and with increasing WO_3 contents. Moreover, this study is extended in order to study the effect of successive gamma irradiation on the UV–Visible absorption spectra and the induced defects generated through the irradiation process. The final goal of this study is to provide further ideas or confirmation about the proper status of bluish colour of tungsten ions present.

Experimental details

Preparation of the glasses

The glasses were prepared from chemically pure raw materials. Lead oxide was introduced as red lead oxide (Pb_3O_4), and P_2O_5 was added in the form of ammonium dihydrogen phosphate ($NH_4H_2PO_4$). Pure WO_3 was used as the source of tungsten. The weighed batches were melted in porcelain crucibles at the temperature of 800 °C for 1 h. The melts were rotated several times, and the homogenized melts were poured in slightly heated stainless steel molds of the required dimensions. The prepared samples were immediately transferred to an annealing furnace regulated at 200 °C. The muffle was switched off after 1 h and allowed to cool to room temperature at a rate of 20 °C/h. Table 1 depicts the chemical compositions of the undoped and WO_3-doped glasses.

Table 1 Composition of lead phosphate glasses

Glass samples	Composition wt%		
	PbO	P_2O_5	WO_3 add. %
Base	50	50	0
1 W	50	50	0.01
2 W	50	50	0.05
3 W	50	50	0.5
4 W	50	50	2.5
5 W	50	50	5

UV–Visible absorption spectral measurements

The optical UV–Visible absorption spectra of highly polished samples of the undoped and WO_3-doped glasses of the dimensions $1 \times 4 \times 0.1$ cm^3 were recorded at room temperature before and after each successive gamma dose by a recording spectrophotometer in the range 200–1100 nm type JASCO, Corp., V-570, Rel-00, Japan.

Infrared absorption measurements

The infrared absorption spectra of the undoped and WO_3-doped glasses were measured at room temperature in the wave number range 400–4000 cm^{-1} by a Fourier Transform computerized infrared spectrometer from JASCO Corp., FT/IR-430, Japan.

The samples were investigated as fine powders which were mixed with KBr in the ratio(2.200 mg glass powder to KBr, respectively). The weighed mixture was then subjected to a pressure of 5 tons/cm^2 to produce clear homogeneous discs. The IR spectra were measured immediately after preparing the discs.

Raman measurements

Raman measurements of some WO_3-doped samples were made for fine glass powder using a Fourier Transform Raman spectrometer (model Nexus 760 Nicolet-Madison, WI, USA) equipped with a 2 W Nd: YAG laser (1064), which eliminates the problem at 0.7 W laser power, 64 scans and 4 cm^{-1} resolution. The samples were measured in the range from 3700 to 100 cm^{-1}).

Gamma irradiation facility

A^{60}Co gamma cell (2000 Ci) was used as a gamma ray source with a dose rate of 1.5 Gy/s (150 rad/s) at a temperature of 30 °C. The investigated glasses were subjected to the same gamma dose every time. Using a Fricke dosimeter, the absorbed dose in glass is expressed in terms of absorbed dose in water, rather than in terms of dose in glass. No cavity theory correction was made.

Electron spin resonance measurements

Electron spin resonance spectra were recorded at room temperature on an ESR spectrometer (Bruker, E 500; Germany) operating at 9.808 Hz and using 100 kHz field modulation. The magnetic field was scanned from 480 to 6480 Gauss. The ESR measurements for some selected WO_3-doped samples were taken as an evidence for the presence of the states of tungsten containing unpaired electrons.

Results

UV–Visible absorption spectra

UV–Visible absorption spectrum of base undoped lead phosphate glass

Figure 1 illustrates the UV–Visible spectrum of the base lead phosphate glass before irradiation. The spectrum reveals strong and broad ultraviolet charge transfer absorption extending from 200 to about 300 nm with its central peak at about 255 nm. The spectrum shows no visible absorption bands. On subjecting the glass to successive gamma irradiation, the intensity of the central peak increases with progressive irradiation accompanied by a marked shift to longer wavelength reaching 250 nm in the final gamma dose. The visible spectrum remains showing no visible bands, but the intensity of the absorption curves shows progressive but slightly lower values with irradiation reaching almost saturation, revealing marked resistance to the effect of gamma irradiation.

UV–Visible absorption of WO_3-doped glasses

Figure 2 illustrates the measured UV–Visible absorption before and after gamma-irradiation of WO_3-doped samples. Before gamma irradiation, the WO_3-doped glass containing 0.05% WO_3 reveals, beside the strong UV absorption as in the undoped glass, an obvious broad visible band centred at about 780 nm. When the concentration of WO_3 reaches 0.5% in the glass, the sample reveals a sharp UV band as shown in the undoped glass with two distinct separate regions of absorption: the first UV region extends from the beginning of measurement with 200 nm up to about 400 nm and comprises five peaks at about 205, 240, 275, 310 and 380 nm. The visible spectral region consists of a very broad absorption band revealing three peaks at about 680, 760 and 870 nm. The previous sample and all the subsequent samples containing higher concentrations of WO_3 exhibit distinct bluish colour. The WO_3-doped glasses containing 2.5% or 5% WO_3 reveal the same spectral characteristic as in the 0.5% sample with two distinct separate UV and visible absorption regions. The visible broad band shows marked splitting to about seven peaks at about 630, 650, 680, 720, 770, 800 and 890 nm.

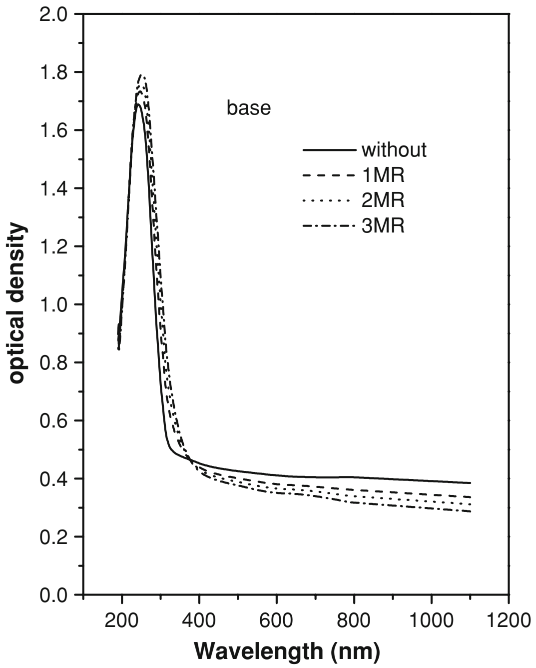


Fig. 1 Absorption spectra of base lead phosphate glass before and after successive ray irradiations

The glass containing the highest WO_3 content (12%) exhibits deep bluish colour and shows extended and continuous or combined UV-visible spectrum revealing peaks at about 240, 320, 350, 380, 420, 480, 660, 780 and 920 nm.

Induced spectra

Figures 3 and 4 reveal the induced spectra of the undoped and WO_3-doped samples which are obtained by subtracting the optical densities obtained from the unexposed specimens from those of the same samples after each specified dose of gamma rays. Thus, the given results express the net results of undoped and WO_3-doped samples showing ΔD, which is the difference in optical density against wavelength for each specimen. The induced spectra are summarized as follows:

(a) *Base undoped glass* Figure 3 illustrates the induced spectrum of the base undoped glass which reveals a strong and wide induced UV band centred at about 300 nm. The intensity of this induced band progressively increases with continuous gamma irradiation.

(b) *WO_3-doped samples* Figure 4 reveals the induced spectra of WO_3-doped lead phosphate glass composition (PbO 50 mol%, P_2O_5 50 mol%) with varying concentrations of tungsten oxide. At low WO_3 content (0.05%), the induced spectra reveal strongly induced UV spectra with two peaks at about 230 and 275 nm. Increasing the WO_3 content to 0.5%, the spectra show extended five high-intense UV-induced bands at about 205, 250, 280, 310 and 385 nm, followed by low and broad visible bands with small peaks at about 640, 680, 720, 820 and 890 nm. When the concentration reaches 2.5% WO_3, the induced spectra show two strong and wide, separate, induced UV bands centred at about 235 and 340 nm, and three

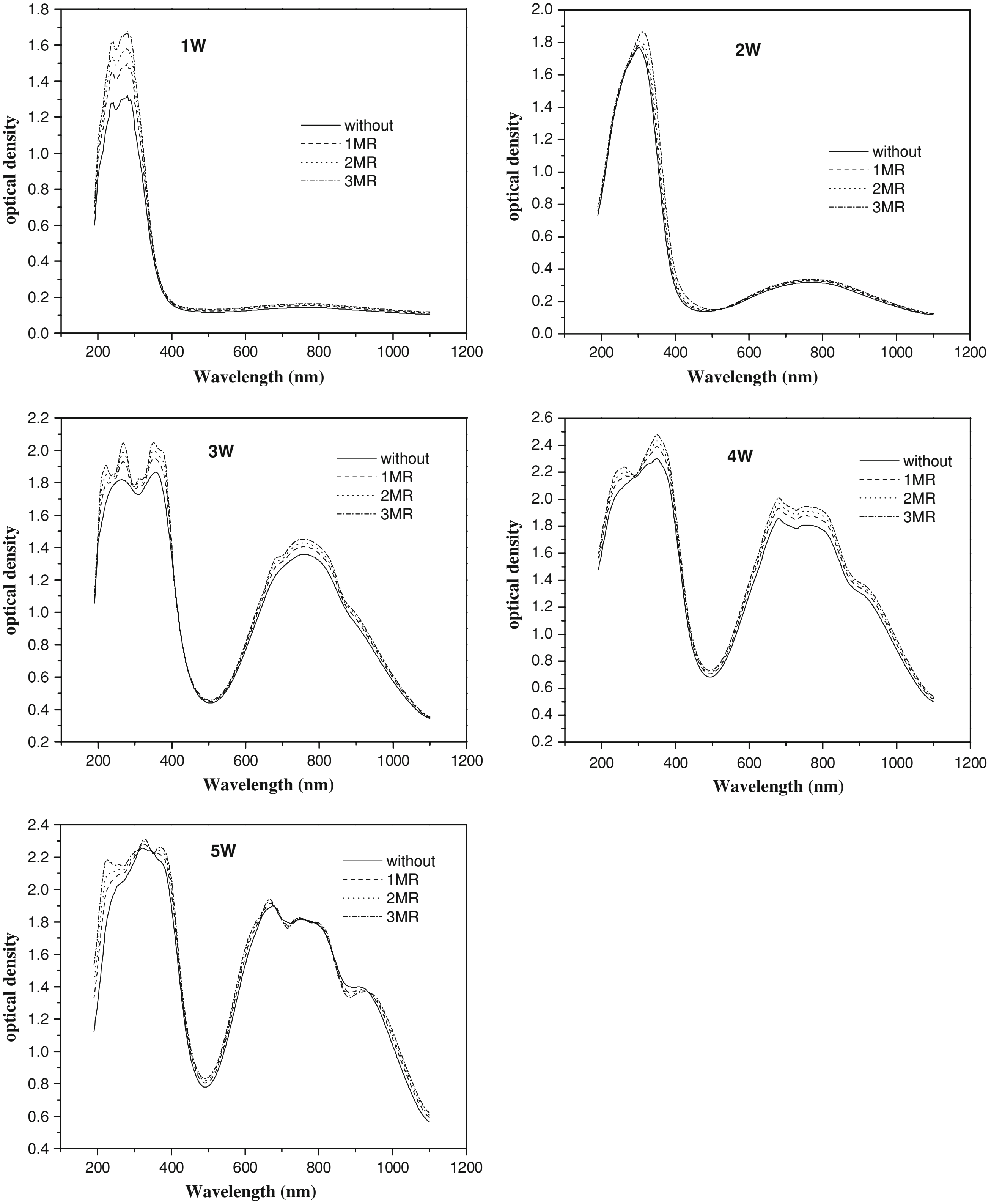


Fig. 2 Absorption spectra of tungsten-doped lead phosphate glass before and after successive gamma ray irradiations

induced broad visible bands centred at about 675, 800 and 940 nm. At high WO_3 content (5% WO_3), the induced spectra reveal extended induced UV–Visible bands beginning with the high band at about 210 nm and followed by very weak peaks at about 280, 340, 380, 420, 600, 670, 690, 730, 840 and 1000 nm.

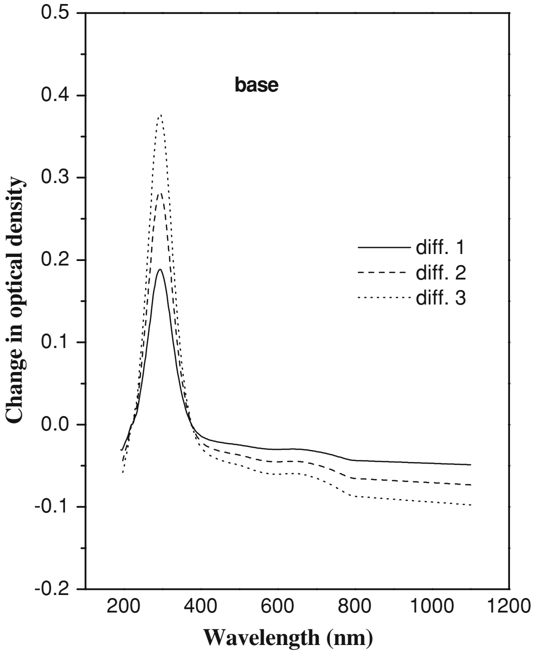


Fig. 3 Induced spectra of base undoped lead phosphate glass

On subjecting the WO_3-glasses to successive gamma irradiation, the following behaviours are observed:

(a) At low WO_3 content (0.05%), the intensity of the absorption bands in the UV region progressively increases with irradiation.
(b) At higher WO_3 content (>0.5%), the intensities of all the induced bands either in the UV or visible regions are observed to slightly but continuously increase with irradiation while the overall spectral curves show resistance to continuous irradiation.

Infrared absorption spectra

Infrared absorption spectrum of base lead phosphate glass

Figure 5 illustrates the infrared absorption spectrum of parent undoped lead phosphate glass. The observed IR spectrum is shown to possess the following characteristics:

(a) A strong IR band with two connected peaks at about 520 and 570 cm^{-1} and with a kink at the ascending lobe at about 430 cm^{-1}.
(b) A medium band with three connected peaks at about 720, 760 and 790 cm^{-1}.
(c) A sharp band at about 950 cm^{-1} and with a kink at the end of the descending lobe at about 1010 cm^{-1}.
(d) A very sharp band with three obvious peaks at about 1110, 1150 and 1190 cm^{-1} and with a peak at the descending lobe at about 1250 cm^{-1}.
(e) A medium sharp band at about 1460 cm^{-1}, followed by a small kink at about 1540 cm^{-1}.
(f) A medium broad band at about 1640 cm^{-1}.
(g) Three sharp bands at about 1740, 2840 and 2940 cm^{-1}.
(h) A near IR broad band with three peaks 3430, 3520 and 3640 cm^{-1}.

Infrared absorption spectra of tungsten-doped glasses

Figure 5 illustrates the IR absorption spectra of WO_3-doped glasses, which indicate the following features:

(a) The introduction of WO_3 up to 2.5% into the host lead phosphate glass causes no obvious changes in the IR absorption spectra. The IR data reveal the persistence of the main phosphate groups vibrations.
(b) At high WO_3 content (12%), the main IR bands due to phosphate network are observed to lose their sharpness and splitting, and the subsidiary bands due to OH and H_2O groups highly decrease in intensity.

Raman spectroscopic measurements

Figure 6 reveals the Raman spectra of three lead phosphate glasses comprising the undoped base ammonium dihydrogen phosphate and two other WO_3-doped glasses containing 0.05% and 5.00%.

The base crystalline ammonium dihydrogen phosphate Raman spectrum consists of a very sharp peak at 921 cm^{-1} and some other medium peaks at 185, 220, 340, 396, 476, 536 and 1657 cm^{-1}, and a final broad band centred at about 3159 cm^{-1}.

The Raman spectrum of the 0.05 WO_3-doped lead phosphate is observed to consist of several component peaks. The spectrum shows a very strong sharp peak at 1147 cm^{-1} and a medium peak at 688 cm^{-1}, and eight small peaks at 213, 306, 462, 501, 945, 1006, 1063 and 1212 cm^{-1}.

Electron spin resonance investigation

Figure 7 illustrates the ESR of the two samples, a base undoped lead phosphate glass showing minor kinks and a tungsten-doped glass (5% WO_3). The spectrum of the W-doped sample reveals high resolution of the resonance indicating obvious paramagnetic resonance.

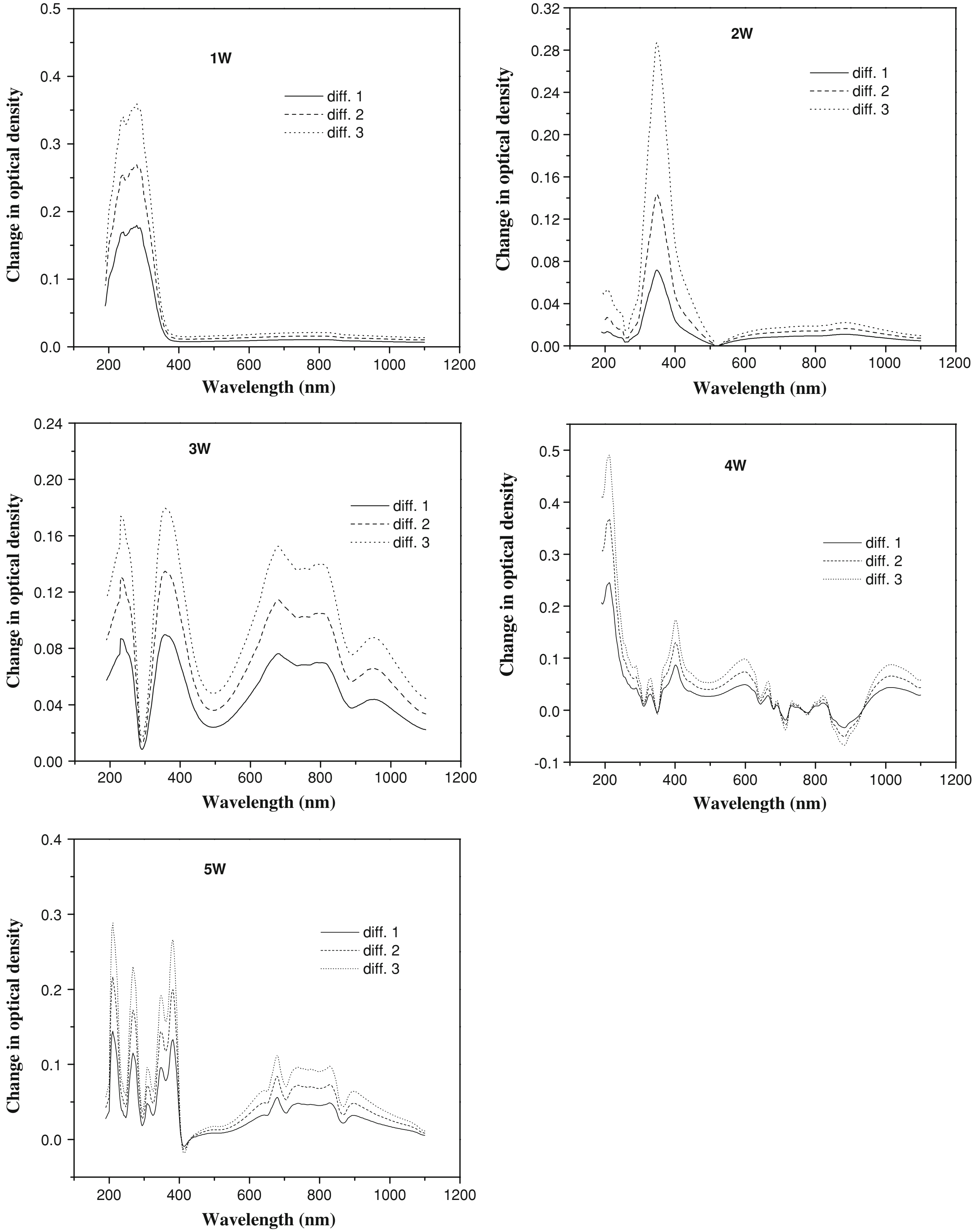


Fig. 4 Induced spectra of tungsten-doped lead phosphate glasses

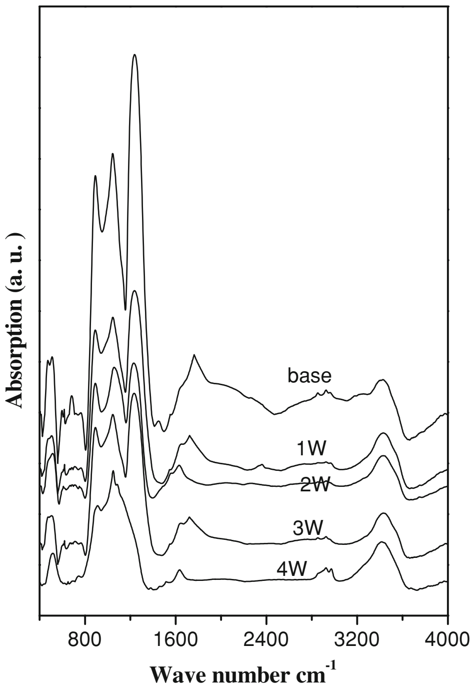


Fig. 5 Infrared spectra of undoped and tungsten-doped glasses

Discussion

Origin of ultraviolet absorption in base lead phosphate glass

It is generally accepted that the UV absorption of the glasses depends on intrinsic and extrinsic effects [14, 15]. The first intrinsic effect is caused by electronic transitions mainly because of the addition of dopants which depends on glass structure and chemical bonding. The second extrinsic absorption is limited by traces of unavoidable impurities in the ppm range, mainly because of the charge transfer transitions of polyvalent ions, such as Fe^{3+} and Fe^{2+}, Cr^{6+} and Cr^{3+}, which are introduced through raw materials and/or melting techniques [14, 16, 17].

Earlier studies by Sigel and Ginther [16] and Cook and Mader [18] have advanced the postulation that charge transfer ultraviolet absorption in commercial glasses originates from the presence of unavoidable trace iron impurities in the raw materials used for glass preparation. Ehrt et al. [15, 17, 19] and ElBatal et al. [20–22] recently have confirmed that charge transfer absorption in the undoped alkali phosphate and borate glasses originates from trace iron impurities mainly as Fe^{3+} ions.

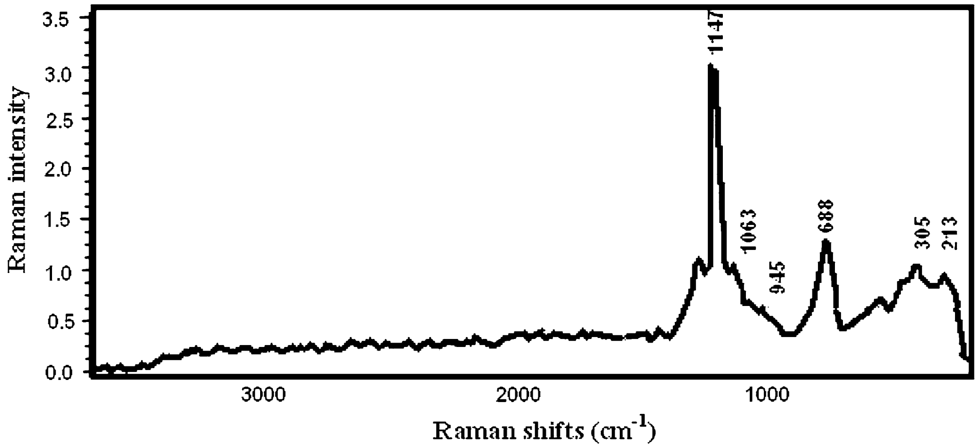
Duffy [14] has assumed that certain metal ions (such as Pb^{2+}, Bi^{3+}, …) absorb radiation through electronic transitions involving orbitals essentially of the metal ions, and the name 'Rydberg' has been suggested for such spectra to distinguish them from the common electron charge transfer spectra. Recent study on lead borate glass [11] has experimentally confirmed this postulation for the sharing of Pb^{2+} ions in the UV spectra of lead borate glass.

It is therefore suggested that the charge transfer ultraviolet absorption observed in the present studied high lead phosphate glass is attributed to the co-sharing of absorption by both trace iron impurities and lead Pb^{2+} ions. The distinction between the spectrum of each species necessitates further study through a combination of techniques and with extra pure materials.

Behaviour of lead phosphate glass as a host medium

It is evident that both lead silicate and lead borate glasses behave like alkali silicate and alkali borate to favour the presence of higher oxidation valence states of the 3d-transition metals [2, 23], while lead phosphate is observed in the present study to resemble alkali phosphate to initiate mainly the lower oxidation states of 3d-TMs. The host base lead phosphate with (PbO 0.5%, P_2O_5 0.5%) compositions is seen experimentally to produce brilliant and deep distinct bluish colour with WO_3-doped glasses. This blue tungsten glass is accepted by various authors [2, 9, 13] as being due to pentavalent tungsten W^{5+} ions, and somewhat resembles

Fig. 6 Raman spectrum of tungsten-doped glass



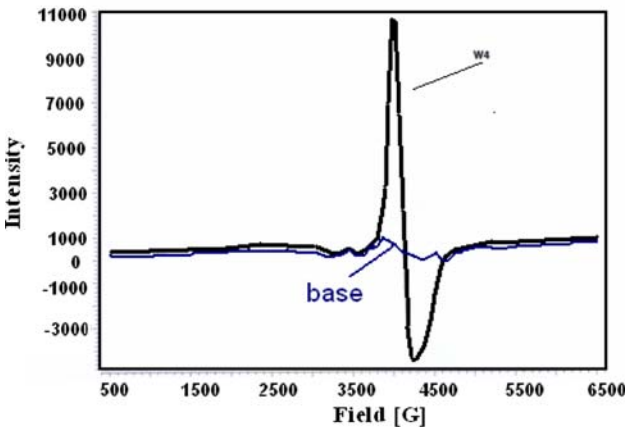


Fig. 7 ESR spectrum of undoped and tungsten-doped glass

the blue bronze in crystalline and thin films of tungsten-doped materials. The same postulation can be attributed to the persistent blue colour in the prepared WO_3-lead phosphate glasses.

With respect to the structure of the host lead phosphate glass, the role of PbO is accepted to be different than the behaviour of alkali metal oxides which act only as network modifiers. Lead oxide is known to be unique because it is able to form glassy materials with B_2O_3 or SiO_2 with very high percent reaching up to $\approx$90% of the content. Lead oxide plays a dual structural role both as network modifier and as a network former. When the stoichiometric composition of PbO and P_2O_5 reaches 1:1, leading to the formation of lead metaphosphate (PbP_2O_6) glass, PbO finds itself in the network firmly settled with 4-oxygen coordination. Thus, the admission of PbO at this stage of composition into P_2O_5 glass leads to structural reorganization. During this formation process, one of the bridging oxygens is connected into one nonbridging oxygen (NBO) for each PbO addition. It is suggested that the structure reveals gradual transformation of the $PO_4{}^{3-}$ units to $PO_3{}^{-}$ groups in lead metaphosphate glass composition [24].

States of tungsten in glasses and origin of blue colouration in lead phosphate glass

Tungsten can exist in various oxidation states (+2 → +6) in its compounds [3]; however, in glasses, tungsten is believed to exhibit hexavalent(W^{6+}), pentavalent(W^{5+}) or tetravalent(W^{4+}) states [2, 4–12]. It was originally assumed that tungsten oxide can from structural units in the glass network itself [7–10]. Different views have been introduced regarding the various tungsten groups existing in glasses, and these views can be summarized as follows:

(a) Some authors [25, 26] believe that WO_4 tetrahedra are the only group present in the tungsten glasses.

(b) Some other authors assume the existence of mixed coordination states made up of both WO_4 tetrahedra and WO_6 octahedra, and even W_2O_7 groups [2].

(c) Few authors [27, 28] are of the opinion that octahedrally WO_6 groups are the only existing units whatever the glass composition.

(d) Some authors [23, 29, 30] assume that tungsten ions participate in the glass network with different structural units such as: WO_4(td) and WO_6(oct) of W^{5+} ions and $(W^{5+}O_3)$(oct) of W^{5+} ions.

The previous observation of blue colour centre in lithium-tungsten borate glass was related to the formation of a complex which is reminiscent of the electrochemically induced tungsten bronze centres [31]. Later, Von Dirke et al. [32] compared the blue tungsten colouration in glass to the colouration of thin WO_3 films and advanced four proposals or models as to be the origin of blue colour in tungsten glasses:

(a) An intervalence charge tungsten transition (ICTT) between W^{5+} and W^{6+} as suggested by Fruchardt et al. [33].

(b) A ligand field absorption (LFA) of $W^{5+}O_3$ molecular orbital states as proposed by Koffuberg and Benko [34].

(c) The formation of polarons as mentioned by Salje and Hoppmann [35].

(d) Polymerization as suggested by Kleperis et al. [36].

Little Flower et al. [20] investigated, by spectroscopic measurements, tungsten ions in $PbO–Sb_2O_3–As_2O_3$ glasses and identified a broad absorption band at about 800 nm, and the ESR study attributed this absorption to the presence of W^{5+} ions. This broad visible band is assumed to be due to the excitation of the W^{5+} ions from $b_2(xy)$ ground state with crystal field parameters around $\Delta = 16{,}000\ \mathrm{cm}^{-1}$ and $\delta = 13{,}000\ \mathrm{cm}^{-1}$ [31].

Based on the previous postulations, the authors assume that the lead phosphate glass favours the presence of appreciable percent of W^{5+} ions in WO_3-doped lead phosphate glass sample, and that further study is needed to specify the detailed spectroscopic state of W^{5+} ions in such glass.

Contribution of the effect of gamma irradiation

It is well-known that, when subjected to ionizing radiation (e.g. γ, UV rays) most glasses acquire radiation-induced defects which may give rise to optical and/or ESR absorption bands [37–39]. The radiation damage processes, which take place in glass, are generally the same as those, which occur in crystals [39]. In the simplest purview, there are three basic processess: (1) radiolysis, (2) displacement (or knock-on) damage, and (3) electron rearrangement. In all the cases, what we define as damage is the existence of post-irradiation local structure (either atomic or electronic) which differs from the structure which was present before irradiation. The investigation of radiation effects may well lead to a better understanding of the intrinsic defects already present within the glass constituent or network structure as well as the effects of extrinsic defects related to the dopants: either introduced or within impurities or contaminations.

Beekenkamp [40] identified four induced bands in alkali phosphate and advanced the following reasoning:

(a) The 2.3 eV (∼540 nm) center which consists of a hole trapped on a pair of NBOs with the alkali having diffused away.
(b) The 2.9 eV (∼420 nm) consisting of a hole trapped by an oxygen ion with the alkali covalently bonded to the oxygen.
(c) The induced band near 5.1 eV (∼245 nm) is correlated with the 4.8 eV, P_2 defect band in P-doped silica, and seems to arise from an electron trapped in an antibonding orbital of a PO_4 unit, which has an analogue in the silicate glasses.
(d) The band at 6 eV (∼200 nm) is due to an oxygen vacancy in a PO_4 tetrahedron which has trapped two electrons.

Later, Archidi et al. [41] identified in alkali phosphate glasses an induced defect based on a hole trapped on a pair of NBOs bonded to a single phosphorus atom. Moreover, additional defect centres are identified which are related to the peroxy linkages –P–O–O–P– and/or –P–O–O–Mo–.

Recent studies by Moncke and Ehrt [19] have identified the formation of 6–9 induced bands in irradiation phosphate glass. These bands are observed in the visible and UV region and assigned to phosphate anions. Three bands are observed in the visible region which are assigned to a phosphate-bonded oxygen hole centers (POHCs), and three bands are related to oxygen hole centers (OHCs), and further three bands within the UV region which are related to electron centers (PECs).

The present experimental UV–Visible absorption indicates that gamma-irradiation of the base undoped lead phosphate glass causes mostly changes in the intensities of the absorption bands especially that on the UV region while the visible region shows resistance to irradiation. This experimental evidence indicates that the lead phosphate possesses the potential to resist gamma irradiation to a measurable extent and that the changes observed in the UV absorption are virtually originating from the presence of trace iron impurities. It is obvious that progressive gamma irradiation generates the released negative electrons and positive holes. It seems that some of the iron species present in the divalent state (Fe^{2+}) capture positive holes through photochemical reactions during the irradiation process. The net result is the formation of trivalent iron (Fe^{3+}) species, and these ions are known to absorb in the UV region, and hence the observed increase in the intensities of the UV region. It is believed that the base host lead phosphate which is constituted with heavy metal ions (Pb^{2+}) in appreciable content (50 mol%). Glasses containing heavy metal ions (e.g. Pb^{2+}, Bi^{3+}…) are known to be potential radiation-resistant candidates, and find applications as radiation-shielding materials [42–46].

A very recent study by Moncke and Ehrt [47] has identified an induced defect at 770 nm in W-doped aluminofluoride phosphate glasses (with WO_3 level 50–5000 ppm), while it is less sensitive in borosilicate. They can confirm the presence of charge transfer bands due to iron impurities although they have used high purity reagents in the preparation of the glasses.

In the WO_3-doped glasses, presently studied, prominent absorption bands could be easily identified before irradiation and are more distinguished with the higher WO_3 content. The absorption bands are easily observed in both the UV and visible regions. The ease of identification of these specific absorption bands seems to be related to the presence of appreciable pentavalent tungsten ions which are stabilized by the presence of high PbO content (50 mol%). Hexavalent chromium colours are known to be stabilized in high lead glasses [2].

The failure or the inefficiency of gamma irradiation effects on undoped and tungsten-doped glasses can be related to the presence of heavy Pb^{2+} ions which retard the formation of extra induced defects. The already observed changes are the slight increases of the intensities of the absorption bands compared to those present before irradiation. The increase in the WO_3 content decreases this effect to a noticeable degree indicating also the shielding behaviour of tungsten ions surplus to the same effect as that of the heavier lead Pb^{2+} ions.

Interpretation of the infrared absorption spectra

In vitreous system, it is assumed [22, 48, 49] that vibrations of the characteristic groups of atoms in the network are independent of the vibrations of other groups. Infrared spectroscopy lends itself as an effective tool, because the techniques are sensitive to short-range ordering and local interactions.

Most researches on the vibrational spectroscopy of phosphate crystals treat information on their structure in terms of oxygen bridges and terminal groups rather than in terms of Q^n species [50, 51]. It is known [52] that both the polar and non-polar vibrations of phosphate lattices are active in both IR and Raman spectra.

The IR spectra are dominated by intense bands related to cation- versus anion-made vibrations whereas the Raman spectra are dominated by intense bands related to modes involving polarizability variations. In general, the assignment of modes in the glasses is done by reference to what is known as the crystalline phases of equivalent composition [50].

It is reported that the strong IR band at about 475 cm^{-1} is assigned to the bending vibrations of O–P–O unit, δ (PO_2) modes of $(PO_3)_n$ chain groups[53], and the connected band at about 512 cm^{-1} is related as a fundamental frequency of $(PO_4)^{3-}$ [54], or as harmonics of P=O bending vibrations [55]. The medium peak at about 725–767 cm^{-1} may be attributed to the symmetric stretching vibration of P–O–P rings [5]. The IR absorption in the region 891 cm^{-1} was found to be sensitive to the different metaphosphate groups in the form of chain-, ring-, and terminal groups [56]. The strong band at about 1043 cm^{-1} is attributed to asymmetric stretching of P–O–P groups, υ_{as}(P=O) modes [51]. The small band at about 1627 cm^{-1} is related to the P–O–H bridges [12–14]. The broad band centred at about 3438 cm^{-1} is attributed to H_2O or POH vibration [57–60].

Experimental IR absorption spectra of WO_3-doped glasses up to the level of 12%, reveal the general maintenance of the main characteristic phosphate network groups, but they show some different features reflecting the depolymerization effect of WO_3 addition on the phosphate network, which can be interpreted as follows:

(a) All the intensities of the main characteristic bands progressively decrease with the increase of WO_3 content.
(b) The appearance of a kink at about 420 cm^{-1}, which seems to be related to W_4 (of WO_6) mode as suggested by Maczka et al. [61, 62].
(c) The sharp bands identified at about 1700, 2820 and 2940 cm^{-1} sharply decreases with the increase of WO_3 content. These bands are related to P–O–H and P–H stretching [58, 60].

Interpretation of the Raman spectra

Raman spectroscopy is accepted as a powerful tool and as an analytical technique, sensitive to define the local or structural units in glasses, such as infrared spectroscopy [63, 64]. Raman scattering spectra have been used for investigation of the molecular or local structure in phosphate glasses [65, 66]. In the Raman spectra of metaphosphate glasses, there are Raman bands, which could be easily identified, 685–695 cm^{-1} for the υ_5(POP) vibration, at 1165–1175 cm^{-1} for the $\upsilon_5(PO_2)$ vibration, and a band at 1270–1285 cm^{-1} for the $\upsilon_{as}(PO_2)$ vibration [65, 66].

The experimental Raman spectra (Fig. 6) can be interpreted on the same previous postulations. The very strong sharp peak at 1143–1147 cm^{-1} to the symmetric stretch of PO_2 vibrations, the medium band to (P–O–P) vibration and the weak band at about 945 cm^{-1} to the W–O stretching vibrations.

Interpretation of the ESR measurement

The ESR spectra illustrated in Fig. 7 reveal that the undoped sample gives no significant resonance but only a small kink. The W-doped sample (5% WO_3) shows high resolution resonance spectrum indicating the dominance of W^{5+} ions because these ions possess unpaired electrons and hence their paramagnetic character. On the other hand, W^{6+} ions possess paired electrons and thus did not share in the experimental ESR spectrum.

Conclusion

UV–Visible absorption spectra of prepared undoped and WO_3-doped local phosphate glasses have been measured before and after successive gamma irradiation. Ultraviolet spectrum of undoped lead phosphate glass reveal strong and wide absorption which is proposed to be related to combined absorption due to of trace iron impurities and lead Pb^{2+} ions. High content WO_3-glasses are coloured blue and exhibit distinct visible bands which indicate the presence of appreciable pentavalent W^{5+} ions in these high lead phosphate glasses. Gamma irradiation is observed to reflect shielding or resistance behaviour by the host high lead phosphate glass which is attributed to the movement of electrons or positive holes in the glass network during the irradiation process. Infrared and Raman spectroscopic data indicate and confirm the presence of metaphosphate units as the main structural units in the lead phosphate glass considered in this study. ESR measurements confirm the presence of pentavalent unpaired W^{5+} ions.

References

1. McMillan PW (1979) Glass-ceramics, 2nd edn. Academic Press, London, p 82
2. Bamford CR (1977) Colour generation and control in glass, glass science and technology, vol 2. Elsevier Scientific Publishing Company, Amsterdam, p 118
3. Cotton FA, Wilkinson G, Murillo CA, Buchmann M (1999) Advanced inorganic chemistry, 6th edn. Wiley, New York
4. Selvaraj U, Rao KJ (1985) J Non-Cryst Solids 75:315

5. Selvaraj U, Kershava Sunder HG, Rao KJ (1989) J Chem Soc Faraday Trans 85:251
6. Muthupari S, Kulkarni GU, Rao KJ (1994) Bull Mater Sci 17:1029
7. Muthupari S, Rao KJ (1996) J Phys Chem Solids 57:553
8. Nadiri A, Yacoubi A, Bih L, Haddad M, Levaseur A (1990) Adv Mater Res 1–2:413
9. Boudlich D, Bih L, ElHassan Archidi M, Haddad M, Yacoubi A, Nadiri A, Eloudi B (2002) J Am Ceram Soc 85:623
10. Poirier G, Poulain M, Messddeq Y, Ribeiro SJL (2005) J Non-Cryst Solids 351:293
11. ElKhshen AA, ElBatal FH, Marzouk SY (2008) Indian J Pure Appl Phys 46:225
12. Haddad M, Nadiri A, Biyadi A, Archidi ME, Folgado JV, Beltran-Porter D (1992) J Alloys Compd 188:161
13. ElBatal FH, Marzouk SY, EzzElDin FM (2009) Physica (B) (under publication)
14. Duffy JA (1999) Phys Chem Glasses 38:289
15. Natura U, Ehrt D, Naumann K (2001) Glastech Ber Glass Sci Technol 74:23
16. Sigel GH Jr, Ginther RJ (1968) Glass Technol 9:66
17. Ehrt D, Ebeling P, Natura U (2000) J Non-Cryst Solids 263& 264:240
18. Cook L, Mader KH (1982) J Am Ceram Soc 65:109
19. Moncke D, Ehrt D (2004) Opt Mater 25:425
20. ElBatal FH, Abo-Naf SM, EzzElDin FM (2005) Indian J Pure Appl Phys 43:574
21. Marzouk SY, ElBatal FH (2006) Nucl Instrum Methods Phys Res (B) 248:90
22. ElBatal FH, ElKheshen AA, Azooz MA, AboNaf SM (2008) Opt Mater 30:881
23. Little Flower G, Sahaya Baskaran G, Krishna Mohan N, Verraiah N (2006) Mater Chem Phys 100:211
24. Dayanand C, Bhikshamaiah G, Tyagaraju VJ, Salagram M, Krishna Murthy ASR (1996) J Mater Sci 31:1945. doi:10.1007/BF00356615
25. Shaltout I, Tang Y, Braunstein R, Abou ElAzm MA (1995) J Phys Chem Solids 56:141
26. Shaltout I, Tang Y, Braunstein R, Shaisha EE (1996) J Phys Chem Solids 57:1223
27. Sekiya T, Mochida N, Ogawa S (1994) J Non-Cryst Solids 176:105
28. Charton P, Cengewbre I, Armand P (2002) J Solid State Chem 16:175
29. Dimitrov V, Arnaudov M, Dimitriev YB (1984) Monatschfte Chem 115:987
30. Subbalakshmi P, Verraiah N (2003) J Phys Chem Solids 64:1027
31. Abdellouhab RM, Braunstein R, Barner K (1989) J Non-Cryst Solids 108:109
32. Von Dirke M, Muller S, Barver K, Rager H (1990) J Non-Cryst Solids 124:265
33. Fruchardt JM, Herve G, Launary J, Massart R (1976) J Inorg Nucl Chem 38:1627
34. Koffuberg FP, Benko FA (1980) J Non-Cryst Solids 40:7
35. Salje E, Hoppmann G (1981) Philos Mag B 43:105
36. Kleperis JJ, Cikmach PD, Lusis AR (1984) Phys State Solidi (A) 83:291
37. Bishay A (1970) J Non-Cryst Solids 3:54
38. Friebele EJ, Griscom DL (1979) In: Doremus RH, Tomozawa M (eds) Treatise on materials science and technology, 17th edn. Academic Press, New York, p 257
39. Friebele EJ (1991) In: Uhlmann DR, Kreidl NJ (eds) Optical properties of glass. American Ceramic Society, Westerville, OH, p 205
40. BeekenKamp P (1965), Thesis, Technical University, Eindhoven
41. Arichidi ME, Haddad M, Naddiri A, Benyaich F, Berger R (1996) Nucl Instr Meth Phys Res B 116:145
42. Ewing RC, Weber WJ, Chinard FW (1995) Prog Nucl Energy 29(1):61
43. Singh H, Singh K, Germand L, Sahota HS, Nathuram R (2002) Nucl-Inst Meth Phys (B) 207:257
44. ElBatal FH, Azooz MA, Ezz ElDin FM (2002) Phys Chem Glasses 43:260
45. Singh N, Singh KJ, Singh K, Singh H (2004) Nucl Inst Meth Phys Res (B) 225:305
46. ElBatal FH (2007) Nucl Instr Meth Phys B 254:243
47. Moncke D, Ehrt D (2006) J Non-Cryst Solids 352:2631
48. Tarte P (1982) Spectrochim Acta 18:467
49. Condrate R (1972) Introduction to glass science. New York, Plenum Press, p 101
50. Nelson BN, Exhahosr GJ (1979) J Chem Phys 71:2379
51. Efimov AM (1997) J Non-Cryst Solids 209:209
52. Moustafa YM, El Egili K (1998) J Non-Cryst Solids 240:144
53. Znacik P, Jamnicky M (1992) J Non-Cryst Solids 146:74
54. Abdel-Kader A, Higazy AA, ElKholy MM (1991) J Mater Electron 5:15
55. Exarhos GJ (1986) In: Warlrafen GE, Revez AG (eds) Strucure and bonding in non-cryst solids. Plenum Press, New York, p 203
56. Chowdari BVR, Tan KI, Chia WT, Gopala Krishnan R (1990) J Non-Cryst Solids 119:95
57. Montagne L, Palrit G, Mairesse G (1996) Phys Chem Glasses 37:206
58. Husung RD, Doremus RD (1990) J Mater Res 25:2209
59. Chahine A, El-Tabirou M, El-Banaisci M, Haddad M, Pascal JL (2004) Mater Chem Phys 84:41
60. ElBatal FH (2008) J Mater Sci 43:1070. doi:10.1007/s10853-007-2254-x
61. Maczka M, Waskomska A, Hmuza J (2006) J Solid State Chem 179:103
62. Maczka M, Maclik B, Hamuza J, Waskomska A (2006) J Non-Cryst Solids 352:5586
63. Wong J, Angell CA (1976) Glass structure by vibrational spectroscopy. Marcel Dekker, New York
64. Kao J, Bae B, Na H (1997) J Non-Cryst Solids 212:173
65. Tallant DR, Nelson C, Wilder JA (1986) Phys Chem Glasses 27:71
66. Morgan SH, Magruder RH, Silberman E (1987) J Am Ceram Soc 70:70