Characterization of WO₃-doped borophosphate glasses by optical, IR and ESR spectroscopic techniques before and after subjecting to gamma irradiation

M A Ouis¹, H A El-Batal¹*, M A Azooz¹ & A M Abdelghany²

¹Glass Research Department, National Research Centre, Dokki, Cairo, Egypt
²Spectroscopy Department, National Research Centre, Dokki, Cairo, Egypt

*E-mail: h_elbatal@yahoo.com

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Borophosphate glasses containing increasing WO₃ within the doping level (0.16-1.33%) have been prepared and investigated by UV-visible, infrared spectral measurements. These glasses have been exposed to gamma rays with a dose of 8 Mrad for studying the effect of gamma radiation on the combined studied spectra of such glasses. The optical spectrum of undoped borophosphate glass reveals strong UV absorption but with no visible bands. This strong UV absorption is related to the presence of unavoidable trace iron impurities within the chemicals used for the preparation of this borophosphate glass. The WO₃-doped samples show two additional UV and visible bands at about 380 and 740 nm due to the presence of both W⁶⁺ and W⁵⁺ ions in noticeable content. The calculated induced spectra reveal the appearance of an ultraviolet band at 320 nm and two visible bands centered at 390 and 540 nm which are related to the combined presence of W⁶⁺ and W⁵⁺ ions. The FTIR spectra show vibrational bands due to characteristic constitutional phosphate and borate groups but the phosphate groups are predominant due to the high P₂O₅ content (50%). The effect of the addition of WO₃ with the dopant level reveals limited changes in the IR spectra. Electron spin resonance (ESR) spectra show specified signals in the high WO₃ content glass but on gamma irradiation the signals are disappeared. This result confirms the decrease of the W⁵⁺ ions by photochemical oxidation to paired W⁶⁺ ions. This result is also observed in optical absorption of WO₃ doped glasses after gamma irradiation through the disappearance of the visible band at 740 nm.

Keywords: Tungsten, Borophosphate glass, FTIR, UV-visible, ESR, Gamma irradiation

1 Introduction

Borophosphate glasses are one of important combined classes of glassy materials as they possess a variety of useful properties. For example, alkali and silver borophosphate glasses have been developed for fast ion conductors, zinc-calcium doped borophosphate glasses found applications as low melting glass solders¹. Several borophosphate glasses exhibit high chemical durability, keeping in view of the fact that borophosphate glasses have attractive applications, chemically more durable compared to both pure phosphate and pure borate glasses². Also, borophosphate glasses are promising materials for optical applications because of their good optical properties, low refractive indices, low dispersion and good transparency from the ultraviolet to the near infrared regions³. In view of these promising and diversified optical properties, these glasses are considered as materials for optical components such as IR domes, optical filters, modulators, memories and laser windows. Furthermore, these glasses may be considered as good materials for hosting lasing ions such as chromium/ rare earth ions since these glasses provide a low photon energy environment to minimize non-radiative losses.

Tungsten is the third element in group VI B (chromium group) of the Periodic Table. It possesses different oxidation states ranging from (0) to (+ VI) in various inorganic compounds⁴. WO₃ has the oxidation state (+VI), its density is higher than Cr and Mo which are found in its group. In a series of previous studies on tungsten doped glasses, it has been indicated that glasses of lead borate with 60% PbO or more promote the presence of dominant percent for hexavalent tungsten ions as evidenced by optical and Raman spectral measurements⁵. On the other hand, both lead metaphosphate (50% PbO, 50% P₂O₅) glass and sodium metaphosphate (50% Na₂O, 50% P₂O₅) glass are observed to favour the presence of tungsten in the pentavalent state in a measurable content as evidenced by combined spectroscopic techniques⁶.

The aim of the present work is to prepare and characterize some sodium borophosphate glasses containing different additives of WO₃ using combined spectroscopic techniques (UV-visible and infrared absorption measurements) before and after exposure
to gamma irradiation. The objective also includes the characterization of the radiation induced spectra and their origin. Electron spin resonance investigations of the highest WO$_3$ content sample have been carried out to justify the states of tungsten ions in the studied glass before and after irradiation.

2 Experimental Details

The glasses have been prepared from chemically pure materials. B$_2$O$_3$ was introduced as H$_3$BO$_3$, P$_2$O$_5$ as NH$_2$H$_2$PO$_4$, Na$_2$O as Na$_2$CO$_3$, and WO$_3$ as it is. Alumina was added as calcinated Al$_2$O$_3$ (0.5%) to prevent liability to devitrification. The weighed batches have been melted in porcelain crucibles at about 1250°C in an electrical furnace for about one and half hour. The melts were rotated at intervals and poured in warmed stainless steel molds for the required dimensions. Then, the prepared samples were immediately annealed at about 400°C in a muffle furnace, which was left to cool over night. The chemical compositions of the prepared glasses are listed in Table 1.

The ultraviolet and visible optical absorption spectra were immediately measured for well polished glass samples of equal thickness (2 mm ± 0.1) before and after gamma rays irradiation in the range 200-900 nm. A recording spectrophotometer (type JASCO-570, Japan) was used for these optical measurements. The infrared absorption spectra were measured at room temperature in the wavenumber range 400-4000 cm$^{-1}$ by a Fourier Transform infrared spectrophotometer (type 5000, Mattson, USA). The samples were pulverized into fine powder, and then mixed with KBr powder with a weight ratio (1:100), respectively. The mixtures were subjected to a load of 5 t cm$^{-2}$ in an evocable die for 2 min to produce clear homogenous discs. The IR measurements were carried out immediately after preparing the discs. The same FTIR spectra were repeated for the same glasses after gamma irradiation with a dose of 8 M rad (8×10$^4$ Gy). A $^{60}$Co gamma cell (2000 Ci) was used as a gamma ray source with a dose rate of 1.5 Gys$^{-1}$ (150 rads$^{-1}$) at a temperature of 30°C. The investigated glasses were subjected to the same gamma dose. Using a Fricke dosimeter, the absorbed dose in water, rather than in terms of dose in glass. No cavity theory correction was made.

Electron spin resonance spectra were recorded at room temperature on an ESR spectrometer (Bruker, E 500; Germany) operating at 9.808 GHz and using 100 GHz field modulation. The magnetic field was scanned from 480 to 6480 G. The ESR measurements were taken for glass powder before and after irradiation as an evidence for the confirmation of the state of tungsten ions containing unpaired electrons.

3 Results

3.1 Optical absorption spectra of undoped borophosphate glass before and after gamma irradiation

Figure 1 shows the optical absorption spectrum of the base undoped glass before irradiation exhibiting broad and strong UV absorption with a main band at about 230 nm with an attachable peak at about 275 nm and no visible bands could be identified. By subjecting this undoped glass to 8 Mrad (8×10$^4$ Gy) of gamma irradiation, the intensity of the UV absorption increases while the rest of the absorption spectral curves remain almost parallel without any obvious changes.

3.2 Optical absorption of WO$_3$-doped glasses before gamma irradiation

Figure 2 shows the optical absorption spectra of the WO$_3$ doped glass samples before irradiation with

![Absorbance (a.u.) vs Wavelength (nm)](image)

Fig. 1 — Optical UV-visible absorption spectra of base undoped borophosphate glass before and after gamma irradiation
gamma rays and the optical results can be summarized as follows:
(a) The WO₃ doped samples reveal the same strong UV absorption band as the undoped sample which also extends up to 300 nm besides showing two extra broad bands at about 380 and 740 nm.
(b) The intensities of the two extra new bands increase gradually by increasing the WO₃ content.

3.3 Optical absorption of WO₃-doped glasses after gamma irradiation
Figure 3 shows the optical absorption of the WO₃-doped glasses after irradiation with a gamma dose of 8 M rad (8×10⁴ Gy). The optical results show some variations than the spectra obtained before gamma irradiation. The extra WO₃ doped band at 380 nm reveals almost constancy in intensity with irradiation while the broad band at about 740 nm is observed to be disappeared with irradiation.

3.4 Induced spectra of the glasses
The induced spectra (Fig. 4) are obtained by subtracting the optical densities obtained from the unexposed samples from that of the same samples after gamma irradiation. Thus, the induced results show the net result of difference in optical densities between undoped and WO₃-doped samples showing ΔD, which is the change in optical density against wavelength.
Inspection of the induced curves in Fig. 4 shows three characteristic absorption bands. A sharp band is observed to be centered at about 320 nm with a slight shift to longer wavelength with increasing WO₃ content in the borophosphate glass. The other two bands are broad and centered at about 390 and 540 nm, respectively.

3.5 Infrared absorption spectra of undoped and WO₃-doped samples before and after gamma irradiation
Figures 5 and 6 show the IR absorption spectra of the base borophosphate glass together with samples doped with varying WO₃ contents before and after exposure to gamma irradiation. The studied glasses show the following FTIR spectral features before irradiation (Fig. 5):
(1) A small band at about 414 cm⁻¹, 485 cm⁻¹, 570 cm⁻¹, 674 cm⁻¹, 736 cm⁻¹.
(2) A broad band ranging from about 800 cm⁻¹ to about 1300 cm⁻¹ which is split to five component peaks at 862, 985, 1050, 1101, 1213, 1290 cm⁻¹.
(3) Finally, a broad band at centered at about 3400 cm⁻¹ is observed.
Figure 5 shows that the addition of WO$_3$ in the doping level investigated (0.16-1.33%) causes minor changes in the IR spectral characteristics. Figure 6 shows that gamma irradiation causes some changes in the positions and intensities of some IR bands which can be summarized as follows:

1. The band at about 570 cm$^{-1}$ is persistent in all studied samples.
2. The peaks within the 600-750 cm$^{-1}$ region are seen to decrease in their intensities.
3. The main band at about 1100 cm$^{-1}$ remains unaffected and becomes the highest intense band.

(4) The band within the range 1270-1320 cm$^{-1}$ is quite indented but shifts to lower wavenumber in the range 1250-1300 cm$^{-1}$.

3.6 Electron Spin Resonance Investigation

Figure 7 shows the ESR of the high WO$_2$ content sample before and after irradiation. It is evident that the glass before irradiation shows characteristic resonance which upon irradiation decreases in intensity.

4 Discussion

4.1 Origin of UV absorption in the undoped borophosphate glass

Many researchers$^7$ have attributed the observed strong charge transfer ultraviolet bands within the optical spectra of numerous commercial glasses to the presence of unavoidable trace iron impurities within the raw materials used for the preparation of these glasses. Duffy$^8$ has recognized and classified differently originated ultraviolet absorption spectra in glasses. Some transition metal ions (e.g. Fe$^{3+}$, Cr$^{6+}$, …) in glasses exhibit characteristic charge transfer ultraviolet absorption bands even if present in the ppm level. Such TM ions in glass owe their UV spectra to an electron transfer mechanism.

Moncke and Ehrt$^9$ have assumed in a series of successive studies on phosphate glasses that small amounts of TM ions and specifically iron impurities (even in the ppm range) cause deterioration of the UV transmission in optical glasses. They have stressed on the need for ultrapure chemicals for the preparation of special optical glasses for recent applications.
Recently El-Batal et al.6,10 have confirmed experimentally that the charge transfer UV absorption bands that are observed in undoped phosphate, borate, and silicate glasses are originated from unavoidable trace iron impurities (mainly Fe$^{3+}$ ions) contaminated within the raw chemical materials used for the preparation of such glasses.

Thus, the observed strong UV absorption observed in the spectrum of the studied undoped borophosphate glass can be related to originate from trace iron impurities (Fe$^{3+}$ ions) contaminated within the raw materials used for the preparation of this borophosphate glass. The same strong UV spectrum is also observed to extend to be observed in the WO$_3$-doped glasses.

### 4.2 Interpretation of the optical absorption of tungsten metal ions in WO$_3$-doped borophosphate glasses

Flower et al.11 have investigated tungsten ions in PbO-Sb$_2$O$_3$-As$_2$O$_3$ glasses by spectroscopic studies and identified that there is a broad absorption band centered at about 800 nm. This broad visible band is assumed to be due to the excitation of the W$^{6+}$ ions from the $b_2$ (xy) ground state with crystal field parameters around $\Delta = 16,000$ cm$^{-1}$ and $\delta = 13,000$ cm$^{-1}$. Tungsten is accepted to be able to exhibit hexavalent (W$^{6+}$), pentavalent (W$^{5+}$) or tetravalent (W$^{4+}$) states in glasses.4,5,24,25 El-Batal et al.6,10 have established by combined optical and FTIR spectral and ESR studies that tungsten ions exist mainly in the hexavalent state (W$^{6+}$) in high lead glasses but in lead phosphate and sodium phosphate glasses the pentavalent state (W$^{5+}$) ions are prevailing.

The observed optical data of the bluish prepared WO$_3$-doped borophosphate samples indicate and confirm that the presence of visible absorption band at about 740 nm can be related to the presence of pentavalent tungsten W$^{5+}$ ions as already observed by several researchers. The observed band at 380 nm is assumed to be due to the presence of hexavalent tungsten W$^{6+}$ ions. This assumption is in accordance with the previous contribution by Moncke and Ehrt12. These researchers have reached the conclusion that 4d and 5d ions including W could absorb strong radiation and as a consequence various extrinsic and intrinsic defects are generated depending on the type of glass and the type of radiation.

### 4.3 Effect of gamma irradiation on glasses

It is accepted that, when subjected to ionizing radiation (e.g. gamma and UV rays) most glasses acquire radiation induced defects which may give rise to optical and/or ESR absorption bands.13-15 The following three processes are expected to operate partly or totally during the irradiation process:

1. Atomic displacement by momentum and energy transfer
2. Ionization and charge trapping
3. Radiolytic or photochemical effects

Previous irradiation studies on phosphate and borate glasses have been summarized in the internationally review articles by Bishay13, Friebele and Griscom14 and Friebele15. Friebele15 has compared the radiation-induced optical absorption spectra in silicate, borate and phosphate glasses. Friebele has observed that the resolution of the spectra of the three mentioned glasses systems reveals that there are three bands near 2.0 to 2.3, 2.9 to 3.0 and 5.1 to 5.5 eV, that are common in all three glasses, while, the 4.0 eV band appears to occur only in the silicate glass.

However, Friebele15 has assumed that, in spite of the obvious similarities in the optical spectra of irradiated alkali borate, phosphate and silicate glasses, the defect centers associated with these bands may not have been completely identical due to the fact that the valence and coordination of the three network formers are different. The response of glasses to gamma rays is related to the rate of formation and accumulation of induced defects during progressive irradiation and hence the production of net characteristic induced damages or colour centers.

### 4.4 Interpretation of the effect of gamma irradiation on optical spectra of WO$_3$-doped borophosphate glasses

The first prominent effect of gamma irradiation is the widening of the UV absorption extending to about 330 nm. The second effect is the very slight decrease of the intensity of the band at about 380 nm which appears to be constant whatever the concentration of WO$_3$ in the glass. The final third effect is the disappearance of the broad band centered at about 740 nm, with progressive radiation. The previous experimental data are explained as follows:

1. It is observed that with gamma irradiation, induced defects are generated within the UV region. This is due to some suggested photochemical reactions leading to the formation of additional Fe$^{3+}$ ions through oxidation of some Fe$^{2+}$ ions present and leading to the increase of the intensity of the UV absorption.
The maintenance of the absorption band at about 380 nm through irradiation which is assumed to be due to the presence of W$^{6+}$ ions. This indicates that the hexavalent tungsten ions are persistent with radiation.

The disappearance of the broad band at about 750 nm related to the presence of W$^{5+}$ ions by gamma irradiation is suggested to be due to the transformation of these pentavalent tungsten ions to lower valence of W$^{4+}$ ions by capturing released electrons or their oxidation to W$^{6+}$ ions. More work is needed to confirm such postulation.

The same results are recently reached by El-Batal and Ouis$^{16}$ on gamma irradiation on tungsten doped lithium phosphate glasses.

4.5 Interpretation of the Infrared absorption spectra

Before interpretation of the FTIR spectra of the studied borophosphate glasses in relation to their structural arrangement, the following points should be considered$^{16,17}:

1. The combination of two mixed oxides as glass-formers, P$_2$O$_5$ and B$_2$O$_3$ in the studied glasses is an interesting subject of study as the two oxides introduce the glassy network with specific and available structural building units.

2. The properties of the mixed oxide glasses are expected to be specific to the prepared mixture, and being distinct of either pure phosphate or pure borate networks.

3. The basic units of pure phosphate glasses are PO$_4$ tetrahedra linked through covalent bridging oxygen atoms, whereas the basic units of borate glasses are trigonal BO$_3$ units.

4. The addition of a modifier oxide to phosphate and borate networks has differing effects.

5. In the phosphate network, it has a depolymerization effect, the extra oxygen atoms introduced by the modifier oxides form negative non-bridging oxygen sites, whose charges are compensated by the positive charges of the modifier cations.

6. In a borate network, the addition of a modifier oxide has the opposite effect, i.e., it increases the degree of polymerization. The boron coordination changes from trigonal to tetrahedral and part of the basic borate units changes from BO$_3$ to BO$_4$ units.

7. In borophosphate glasses, the mixed coordination polyhedral units within the network are likely to be formed by a combination of units based on phosphorous and boron atoms$^{17,18}$.

8. In the basic borophosphate glass investigated, the P$_2$O$_5$ content is higher (50%) than the B$_2$O$_3$ content (30%). Therefore, the vibrational signals are expected to arise mainly from the phosphate network, with some expected contributions from the vibrations of the borate network.

In vitreous system, it is assumed that$^{6,10}$ 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 this technique is known to be sensitive to short-range ordering and local interactions.

Regarding the infrared spectra of the pure phosphate glasses and crystals$^{6,10,18,19}$, it is assumed that the IR band at about 1300 cm$^{-1}$ is ascribed to asymmetric stretching vibrations $v_a$(PO$_2$) of non-bridging oxygen in phosphate chains, whereas another broad band at about 920 cm$^{-1}$ belongs to the asymmetric vibrations $v_a$(P-O-P) of bridging oxygen atoms in phosphate chains. Another band in the IR spectra at about 1080 cm$^{-1}$ is ascribed to the symmetrical stretching vibrations of v$_s$(PO$_2$) and weaker bands in the 720-800 cm$^{-1}$ are assigned to symmetrical stretching vibrations v$_s$(P-O-P) of the bridging oxygen atoms. The broad band at about 500 cm$^{-1}$ belongs to bending vibrations of basic structural units of phosphate glasses$^{6,10,19,20}$.

4.6 Interpretation of the infrared absorption spectrum of the undoped sodium borophosphate glass

On the basis of previous consideration, the following interpretations are introduced:

a. The broad band at around 3446 cm$^{-1}$ is due to the symmetric stretching of O-H groups, or (H-O-H). This band is quite evident because of the hygroscopic nature of phosphate anions and of pulverized powders during the preparation of KBr discs in general.

b. The bands in the region between 1400-1150 cm$^{-1}$ are characteristic of vibrations of both non-bridging PO$_2$ groups and sharing of vibrations of BO$_3$ groups.

c. The bands in the region around 1150-800 cm$^{-1}$ are characteristic of collective terminal P-O and PO$_3$ groups, and the sharing of stretching vibrations of tetrahedral BO$_4$ groups.

d. The bands at about 680-750 cm$^{-1}$ are assigned to asymmetric stretching of the bridging oxygen atoms bonded to a phosphate atom in a Q$^2$ phosphate tetrahedron, and sharing of bending vibrations of B-O linkages in the borate network.
The bands at around 500-582 cm\(^{-1}\) can be ascribed to deformation modes on bending vibrations of P-O.

The band at 348-405 cm\(^{-1}\) is due exclusively to the phosphate network.

4.7 Interpretation of the ESR result

It is obvious that before irradiation, the observed resonance can be attributed to the presence of unpaired electron in which in this case is the pentavalent tungsten ions. On irradiation, the resonance decreases because the pentavalent state is photochemically oxidized to hexavalent tungsten ions which belong to d\(^{0}\) configuration giving no signal.

5 Conclusions

Undoped and WO\(_3\)-doped glasses of the basic composition P\(_2\)O\(_5\) 50\%, B\(_2\)O\(_3\) 30\%, Na\(_2\)O 20\% with different WO\(_3\) contents were prepared. Optical spectrum of undoped borophosphate glass reveals strong UV absorption which is related to the presence of unavoidable trace iron impurities. WO\(_3\)-doped samples show the same UV absorption as the undoped sample beside the resolution of two extra bands at about 380 and 740 nm. The first UV band at 380 nm is related to the presence W\(^{6+}\) ions and the second visible broad band at 740 nm is correlated with the presence of W\(^{5+}\) ions. Infrared spectra are assumed to consist of specifically characteristic vibrations of phosphate units constituting the main component with the sharing of interlinked borate units. The addition of WO\(_3\) within the doping level exerts minor effects on the characteristic vibrational bands.

Gamma irradiation is observed to reveal some effect on the optical spectra of WO\(_3\)-doped glasses. The effect includes the slight decrease of the intensity of the bands together with the almost disappearance of the broad visible band due to W\(^{5+}\) ions. This behaviour is related to the shielding effect of tungsten ions and the combined reduction of W\(^{5+}\) ions to W\(^{4+}\) ions or oxidation to WO\(^{6+}\) ions by suggested photochemical reactions during the irradiation process. This behaviour is related to the shielding effect of tungsten ions and the combined reduction of W\(^{5+}\) ions to W\(^{4+}\) ions or oxidation to WO\(^{6+}\) ions by suggested photochemical reactions during the irradiation process.

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