

Gamma rays Interactions with Bismuth Phosphate Glasses Doped with 3d Transition Metal Oxides

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Abstract Bismuth phosphate glasses of the basic composition (Bi_2O_3 30 mol%– P_2O_5 70 mol%) with additional dopants 3d TM oxides (0.2 wt%) were prepared by the melting and annealing technique. Combined optical (UV/vis.) and FT infrared absorption spectra were measured for the prepared samples before and after gamma irradiation with a dose of 8 Mrad (8×10^4 Gy). Optical spectra reveal strong UV absorption bands due to trace iron impurity together with an additional absorption band due to Bi^{3+} beside characteristic absorption related to specific 3d TM ions with preference for the lower valences due to the reducing effect of phosphate host glass. FTIR spectra show vibrational bands due to phosphate chains with the sharing of absorption bands due to Bi–O vibrations. Gamma irradiation causes limited changes due to the presence of heavy metal Bi^{3+} ions which show some shielding behavior towards gamma irradiation as revealed by optical and FT infrared absorption measurements. Some suggested photochemical reactions are forward to interpret the changes in the UV spectra beside the formation of an induced phosphorus oxygen hole center (POHC) in the visible region.

Keywords Bismuth phosphate glass · Optical · FTIR · 3d TMs · Gamma irradiation

1 Introduction

Phosphate glasses represent a special interesting vitreous system which has been extensively studied for their unique optical and thermal properties beside their ease of melting at lower temperatures [1, 2]. The additions of multivalent oxides to phosphate glasses are accepted to promote promising chemical durability and lead iron phosphate glasses have been recommended as host candidate for burial of some radioactive wastes [3]. Moreover, phosphate glasses have been applied as laser candidate, biocompatible biomaterials, sealing glasses and many valuable applications such as agriglass fertilizer [4–6].

Glasses containing Bi_2O_3 have been of special optical properties [7–10]. Bi_2O_3 is considered to be a conditional oxide which can form extended glass-forming regions with B_2O_3 and SiO_2 in which it is assumed that bismuth ions can form BiO_6 and/or BiO_3 and form stable glasses resembling PbO . These Bi_2O_3 -containing glasses exhibit high refractive index together with high-energy gap attributable to the high polarizability of Bi_2O_3 , which promotes their use in mid spectral rays from UV up to IR [8]. Glasses containing high content of Bi_2O_3 have been identified as suitable candidate for protection from gamma ray irradiation especially being non-toxic and thus can safely replace high lead glasses [9, 10].

Glasses containing 3d TM ions are known to exhibit variable optical, magnetic and electrical properties according to the specific percent of TM ions, condition of melting and the possible presence of some of the transition metal in two or more valence or coordination states [11–13]. It has been

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observed that alkali borate and alkali silicate glasses, generally favor the presence of TM ions in their high valence state or tetrahedral coordination while both alkali phosphate and lead phosphate glasses show the reverse by the identification of the lower valence state or the octahedral coordination [14–16].

When glasses are subjected to ionizing radiation (e.g. γ -ray, UV-radiation), the expected principle effects result mainly from electronic processes [17–19]. Electrons are excited to leave their positions and move through the glass network. For each ionized electron, one electron deficient region and positive hole center is formed. Induced absorption bands identified are due to centers formed by electron trapping (EC) or positive hole trapping (HC). The presence of heavy metal oxides (e.g. PbO, Bi₂O₃, BaO) is found to cause some shielding effects towards gamma irradiation [8–10]. Also, some transition metal ions doped-glasses (e.g. Cu²⁺, V⁵⁺) are observed to retain their spectral optical curves on their position without any changes after gamma irradiation [20, 21]. Because of the ability of TM ions to capture released electrons or positive holes leading to the modification of their valance.

The main objective of the present work is to investigate collective optical and FTIR spectra of un-doped and 3d TM ions-doped (0.2 wt%) host bismuth phosphate glasses of the main chemical composition (30 mol% Bi₂O₃-70 mol% P₂O₅) before and after gamma irradiation. The combined spectral studies are expected to give clear views about the valence state of 3d TM ions in the host bismuth phosphate glass and the detailed picture of the structural building groups in the glass network and the effects of gamma irradiation on the studied combined spectral properties.

2 Experimental Details

2.1 Preparation of the Glasses

Binary bismuth phosphate glasses were prepared from chemically pure materials including ammonium dihydrogen phosphate (NH₄H₂PO₄) for P₂O₅ and bismuth oxide was introduced in the form (Bi₂O₃). The 3d transition metals were added (0.2 wt%) of the following respective oxides: (TiO₂, V₂O₅, Cr₂O₃, MnO₂, Fe₂O₃, CoO, NiO and CuO).

The accurately weighed batches were melted in porcelain crucibles. The batches were heated for 0.5 h at 500 °C to expel ammonia and water vapor and then the electric furnace (SiC rods, Vecstar UK) was raised to 1100 °C to complete mixing and reach acceptable homogeneity through rotating the melts every 30 minutes and the melting time extended to 90 minutes.

The melts were then cast into slightly warmed stainless steel molds and the prepared samples were immediately

transferred to an annealing muffle regulated at 280 °C to release stresses or strains.

The muffle was left to cool after 1 hour to room temperature at a rate of 30 °C/hour.

2.2 Methods and Techniques for Properties Measurements

Optical absorption spectral measurements were carried on polished samples (2mm \pm 0.1mm) using a recorded spectrophotometer (type JASCO V/630, Japan) covering the range from 200 to 1100 nm. The samples after being subjected to gamma irradiation were re-measured.

The infrared spectra of the powdered samples were measured at room temperature in the wavenumber range 400–4000 cm⁻¹ by (FTIR 4000 JASCO, Japan) using the KBr disc technique. The prepared transparent discs measured immediately after their preparation and the same measurements repeated after the powders were irradiated.

An Indian ⁶⁰Co gamma cell (2000Ci) was used as a gamma ray source with a dose rate 1.5 Gys⁻¹ (150 rad s⁻¹). All samples were subjected to a total gamma dose of 8 M rad.

3 Results

3.1 Optical Absorption Spectra

Figure 1 reveals the optical absorption spectra of the base un-doped binary bismuth phosphate glass before and after gamma irradiation. The optical spectrum before irradiation shows strong and wide UV absorption extending from 200 to 360 nm and revealing two distinct peaks at about 245 and 300 nm and followed by a small peak at 380 nm and with

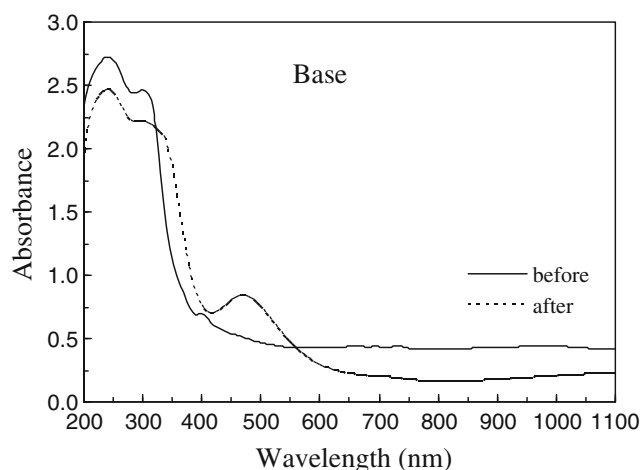


Fig. 1 Optical absorption spectra of binary Bi₂O₃-P₂O₅ glass before and after gamma irradiation

no further absorption to the rest of measurement at 1100 nm. Upon gamma irradiation with a dose of (8 M rad), the UV absorption slightly decreases in intensity and the second strong peak is shifted to about 350 nm and with a generation of a new induced visible broad band centered at about 450 nm.

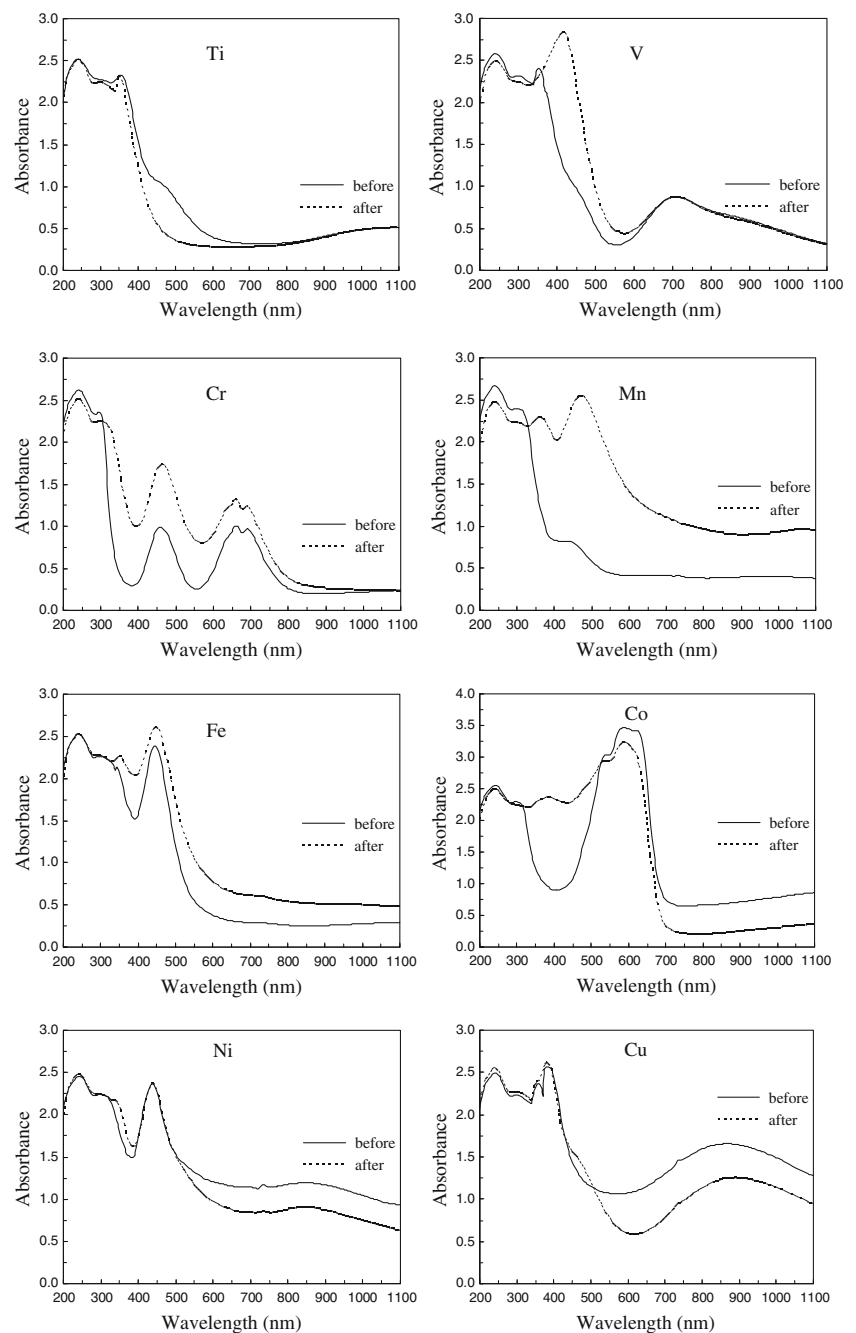
Figure 2 illustrates the optical absorption of 3d transition metals-doped glasses before and after gamma irradiation and the spectral results can be summarized as follows:

a) *Titanium-doped glass*

This titanium-doped glass reveals an optical spectrum consisting of strong and wide ultraviolet absorption with three peaks at 240,300 and 350 nm and with a curvature peak at about 460 nm and with no further absorption to the end of measurement at 1100 nm. Upon gamma irradiation, the spectrum shows the same UV absorption as identified without any variation and the visible curvature at 460 nm is disappeared with the same rest spectrum as that before irradiation.

b) *Vanadium-doped glass*

Fig. 2 Optical absorption spectra of 3d TM ions-doped $\text{Bi}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses before and after gamma irradiation



The V-doped glass exhibits before irradiation strong wide UV absorption extending from 200 to 390 nm with three peaks at about 240, 310 and 380 nm and followed by a curvature peak at about 450 nm and a final broad visible-near IR band extending from 590 to 1100 nm with a peak at about 720 nm and with a small curvature at about 890 nm.

After gamma irradiation, the UV absorption remains almost unchanged and with an extra stronger band at about 450 nm and the broad visible-near IR band also remains unchanged

c) *Chromium-doped glass*

This chromium-doped glass shows before irradiation strong UV absorption with two distinct peaks at about 240 and 310 nm and followed by two consecutive broad visible bands, the first is centered at about 460 nm and the second band with three split peaks at about 600, 650 and 720 nm.

After gamma irradiation, the UV absorption slightly decreases in intensity with shifting of the second peak to about 350 nm and the two visible bands exhibit higher intensities but with almost the same positions of the peaks.

d) *Manganese-doped glass*

The spectrum of the Mn-doped glass reveals a strong UV absorption with two distinct peaks at about 240 and 310 nm and followed by a small peak at about 450 nm and no further bands are identified.

Upon gamma irradiation, the UV absorption slightly decreases in intensity and the appearance of two subsequent strong visible bands centered at about 440 and 540 nm.

e) *Iron-doped glass*

The Fe-doped glass shows before irradiation a spectrum consisting of strong UV absorption with three peaks at 240, 290 and 320 nm and followed by a distinct sharp band with a peak at about 450 nm and without further absorption to the end of measurement at 1100 nm.

Upon gamma irradiation the UV absorption remains almost unchanged but with increase of the intensities of both bands at 380 and 450 nm.

f) *Cobalt-doped glass*

This Co-doped glass reveals before irradiation two strong and broad UV absorption bands with peaks at about 240 and 320 nm and the visible absorption shows strong absorption with two distinct peaks at 540 and 630 nm.

With gamma irradiation, the two UV and visible absorption is observed to be connected with an additional induced band at about 380 nm and the rest of the spectral curve remains parallel to that before irradiation but with lower intensity.

g) *Nickel-doped glass*

The Ni-doped glass shows a spectrum before irradiation consisting of strong UV absorption with two distinct UV peaks at 240 and 320 nm followed by a sharp visible band with peak at about 430 nm and a small peak at 720 nm with broad curvature centered at about 850 nm.

Upon gamma irradiation, the whole spectrum remains parallel with lower intensity with only slight shifting of the second UV peak to 340 nm and the visible curve decreases in intensity but in parallel behavior.

h) *Cu-doped glass:*

The Cu-doped glass reveals before irradiation a spectrum consisting of strong UV absorption with four peaks at about 240, 310, 350 and 380 nm followed a very broad visible-near IR band extending from about 600 to 1100 nm centered at about 820 nm.

With gamma irradiation, the UV absorption remains unchanged but the visible spectrum decreases in its relative intensity with parallel behavior.

3.2 FT Infrared Absorption Spectra

Figure 3 illustrates the collective FTIR spectra for the undoped binary bismuth phosphate glass and that for 3d TM ions-doped samples. The IR spectral curves appear very similar or repetitive in all their vibrational bands and the spectral features can be summarized as follows:

- A far-IR broad and medium band is identified with a peak at 494 cm^{-1}

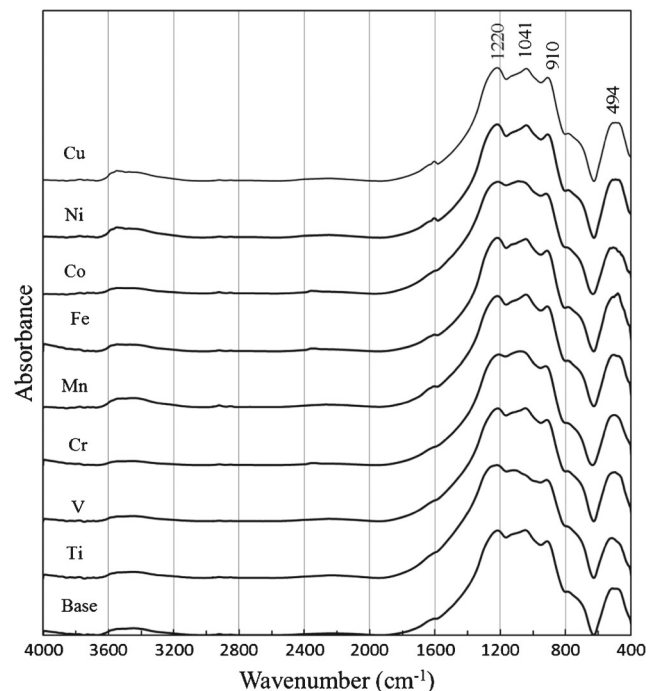


Fig. 3 FTIR absorption spectra for studied glasses

- b. A medium band is observed at about 740 cm^{-1} .
- c. A very broad and highly identified wide band is observed extending from 850 to 1550 cm^{-1} with three distinct peaks at 910 , 1041 and 1220 cm^{-1} .
- d. A small peak is observed at 1640 cm^{-1} .
- e. A near IR broad small band centered at about 3450 cm^{-1} is observed.

All the 3d TM ions-doped glasses show the same IR spectral details as that for the undoped bismuth phosphate glass. The most characteristic features of all the studied glasses are the presence of composite or broad spectra within the wavenumber range 400 to 1550 cm^{-1} revealing interfering or superimposed vibrational bands which needs to be deconvoluted to their individual bands.

3.2.1 Deconvoluted Spectrum of the Base Undoped Bismuth Phosphate Glass

The obvious both similarity and the appearance of overlapping or composite vibrational bands within the wavenumber range 1600 – 400 cm^{-1} initiate conducting a deconvoluted analysis to repetitive FTIR spectrum of the undoped glass.

Figure 4 describes the obtained deconvolution analysis which appears to give more information about the structural

groups either hidden or overlapped and the results reveals specified positions of vibrational bands associated with network structure.

4 Discussion

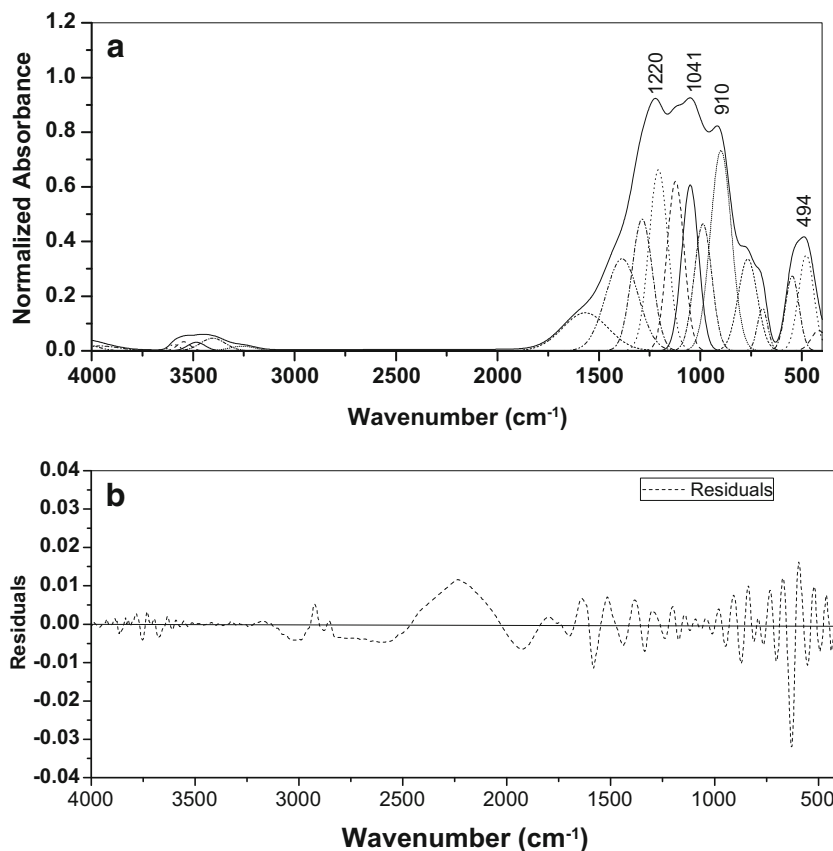
4.1 Interpretation of the Optical Spectra

4.1.1 Interpretation of the Optical Spectra of un-doped Binary Bismuth Phosphate Glass

The optical spectrum of the un-doped sample before irradiation reveals strong UV absorption with two distinct peaks at about 240 and 300 nm and followed by a small peak at 420 nm and with no further absorption bands. The identified strong UV absorption can be related to the absorption of trace iron impurity (mainly Fe^{3+}) present in the chemicals used for the preparation of such base bismuth phosphate glass.

Several glass scientists [22, 23] had previously identified and reached to the same conclusion for the appearance of strong UV absorption in many undoped commercial glasses. Duffy [24] has classified charge transfer spectra frequently observed in many un-doped glasses. He has claimed

Fig. 4 Deconvoluted spectrum of undoped binary bismuth phosphate glasses (a) and (b) residuals of deconvoluted normalized FTIR absorption spectrum of the undoped glass



that many trace metal ions (e.g. Fe^{3+} , Cr^{6+}) when present in glasses even in the ppm level impart charge transfer absorption due to electron transfer mechanism.

Ehrt et al. [25, 26] and El Batal et al. [16, 20, 27] have separately identified strong UV absorption bands in various phosphate and fluorophosphate glasses and have attributed their appearance to trace ferric ions and stressed for the need of ultrapure chemicals to prepare special optical glasses to avoid loss of transmission in recent optical glasses.

Duffy [24] has further added that certain other metal ions including Ce^{3+} , Tb^{3+} , U^{4+} as well as $d^{10}s^2$ ions (such as Pb^{2+} and Bi^{3+}) absorb radiation through electronic transition involving orbitals essentially of the metal ion only, and the name “Rydberg” has been suggested for such spectra to distinguish them from the common charge electron transfer spectra. Optical spectral studies by Sanz et al. [28] and El Batal [29] have assumed that the UV-near visible bands in the range 350–450 nm observed in Bi_2O_3 -containing glasses are correlated with absorption from Bi^{3+} ions.

In conclusion, we can assume that the first two UV peaks at 240 and 300 nm are correlated with absorption of traces iron impurity (mainly Fe^{3+} ions) while the small peak at about 420 nm can be related to absorption of Bi^{3+} ions.

4.1.2 Interpretation of the Optical Spectra of 3d TMs Doped Bismuth Phosphate Glasses

Before interpretation of their spectral results, it must be recognized that the states of the 3d TM ions depend primarily on the type and composition of the host glass and also on melting condition. It has been established [11, 23] that alkali phosphate and lead phosphate glasses generally favor the lower oxidation state or octahedral coordination of the 3d TM ions- doped in glasses. The studied host glass is the bismuth phosphate glass with the nominal chemical composition Bi_2O_3 30 mol%- P_2O_5 70 mol% and therefore it is expected that the lower valences of TM ions or octahedral forms are dominant.

(a) *Titanium-doped glass*

Titanium ions can exist in glasses into two valence states, the trivalent and tetravalent states [11, 13]. Ti^{3+} ion belongs to the $3d^1$ configuration and hence exhibits a single unique visible absorption band at 450–540 nm while Ti^{4+} ion belongs to d^0 configuration and as such will not give d-d visible absorption but exhibits an ultraviolet absorption band.

The optical absorption before irradiation of this sample shows strong UV absorption with three peaks at about 240, 310 and 390 nm beside a distinct curvature at about 450 nm. The first two peaks are related to trace ferric ions present as impurities and the third UV peak can be related to the absorption of Bi^{3+} ions while the visible curvature

is correlated with Ti^{3+} ions [11, 13]. In this TiO_2 doped glass, the low valence state of titanium ions is identified by its specific visible absorption beside UV absorption due to absorption of both (Fe^{3+} , Bi^{3+} ions). Upon gamma irradiation, the whole spectrum before irradiation almost remains after irradiation with the disappearance of the curvature at 450 nm. This behavior can be related to some shielding effect of titanium ions towards gamma irradiation including photo oxidation of Ti^{3+} ions to capture positive hole and then converted to tetravalent Ti^{4+} ions which did not possess any d-d absorption. The same behavior has been reached by previous studies [29, 30].

(b) *Vanadium-doped glass*

The vanadium ions are the unique from 3d TM ions, which can exist in glasses in three possible valences, the trivalent, tetravalent and pentavalent states [11, 23]. The optical spectrum before irradiation reveals strong UV absorption due to collective absorption of trace iron impurities and Bi^{3+} ions beside a curvature at about 450 nm and a new broad band with a peak at about 700 nm and a small curvature at 860 nm. The extended broad visible band is correlated with the collective presence of the two lower valence vanadium ions including mixed trivalent and tetravalent states [11, 21, 23]. Gamma irradiation produces extra-induced band at about 430 nm but the rest of the spectrum remains very close to that before irradiation. It is assumed that this extra induced visible band can be related to the formation of phosphorus oxygen hole center (POHC) or nonbridging oxygen hole center (NBOH) as suggested by Bishay [17], Friebele [18] and Ehrt [19] while the rest of the spectrum reveals some shielding or stability of V_2O_5 -containing glass towards gamma irradiation as assumed by some authors [8, 21].

(c) *Chromium-doped glass*

Chromium ions are known to be able to exist in glasses in two valence states, the trivalent and hexavalent states [11, 23]. The experimental optical spectrum before irradiation reveals strong UV absorption with two peaks at about 240 and 310 nm and followed by two broad visible bands, the first is centered at about 450 nm while the second band exhibits three peaks at about 620, 650 and 720 nm. The two strong UV peak are related to absorption of ferric ions as the un-doped sample and the two other visible broad bands are correlated with octahedrally coordinated low trivalent chromium ions [11]. The absorption of Bi^{3+} ions seem to be overlapped by the absorption of Cr^{3+} ions.

Gamma irradiation causes a small decrease of the UV absorption with shifting of the second peak to longer wavelength but the two visible broad bands show obvious increase in intensity with parallel curve to that before irradiation. This effect can be explained as follows:

- (i) Some of the present ferrous iron ions capture positive holes and are transformed to additional ferric iron ions with the same characteristic UV peak sites.
- (ii) Some of the present few hexavalent chromium ions capture electrons and are transformed to induced additional trivalent chromium ions causing the increase of their intensities in their specific visible sites.

(d) **Manganese-doped glass**

The manganese ions are accepted to be able to exist in two valence states in glasses, the divalent and trivalent forms [11, 23]. The optical spectrum of this glass before irradiation, exhibits strong UV absorption with two peaks at about 240 and 310 nm followed by a medium visible peak at about 460 nm and a small kink at about 720 nm. The experimental UV spectrum can be related to trace iron impurities and the peak at about 460 nm is correlated with the absorption of Bi^{3+} ions and sharing of some trivalent manganese ions. Upon gamma irradiation the UV spectrum is broadened with the appearance of three peaks at 240, 310 and 380 nm followed by a distinct broad band centered at about 460 nm. This behavior upon gamma irradiation can be explained as follows:

- (i) A suggested photochemical reaction can be introduced between some ferrous ions and positive holes to form induced additional ferric ions increasing the extension of UV absorption to further new sites for induced bands.
- (ii) A further suggested photochemical reaction leading to the transformation of some divalent manganese ion to trivalent manganese ions leading to the increase of its characteristic peak in the visible region.

(e) **Iron-doped glass**

It is accepted that iron ions can generally exist in glasses in two valences the divalent Fe^{2+} (d^6) and the trivalent ions Fe^{3+} (d^5) [11] and Sigel [23] has stated that iron is universally present in almost all oxide glasses as trace impurity, and is responsible for the undesirable greenish tint of many commercial glasses. Fe^{2+} ions exhibit a broad strong visible near IR absorption centered at about 1100 nm, which extends into the red, producing the characteristic blue-green of some iron containing glasses. On the other hand, Fe^{3+} ions produce strong UV absorption related to strong charge transfer electron mechanism even if present in the ppm level. In some instances, two main peaks identified at 380 and 420 nm when the traces iron impurity is further slightly increased.

The observed Fe-doped glass shows three strong peaks at 240, 290 and 320 nm which are related to presence of iron impurity (mainly Fe^{3+} ion) [11, 23] while the distinct band at about 450 nm can be related to contribution of both

Fe^{2+} and Fe^{3+} as indicated by Bishay and Kinawi [31] and Edwards et al. [32] in phosphate medium and also the sharing of absorption from Bi^{3+} ions.

Upon gamma irradiation, the UV absorption remains stable while the bands at 380 and 450 nm increase in intensity. This result can be related to photoionization process of some of the divalent iron ions present in the host reducing host glasses and the capturing of positive holes to be converted by photo oxidation to additional $(\text{Fe}^{2+})^+$ or (Fe^{3+}) as suggested by Bishay [17], Friebele [18] and Moncke and Ehrh [33].

(f) **Cobalt-doped glass**

Cobalt is found only as divalent Co^{2+} ions (d^7) in oxide glasses [11, 23] in two coordinations, the octahedral and tetrahedral and the ratio of each of them depends on composition of glass and condition of melting. Bamford [11] identified a band at 520–550 nm and a near IR band at 1200 nm in low alkali glasses which are attributed to octahedral coordination of Co^{2+} ion. The high alkali glasses exhibited two triply split bands near (550, 590 and 650nm) which are indication of the tetrahedral coordination of Co^{2+} ions.

The observed UV peaks are related to trace iron impurity and the high intense split broad visible band is due to tetrahedral coordination of Co^{2+} ions. Gamma irradiation produces extra strong peak at about 380 nm which can be related to photo oxidation of some Fe^{2+} ions to capture positive holes during the irradiation process and are converted to additional $(\text{Fe}^{2+})^+$ or (Fe^{3+}) ions as suggested by various authors [11, 23, 33].

(g) **Nickel-doped glass**

Nickel is normally present in oxide glasses as Ni^{2+} (d^8). Glasses containing Ni^{2+} ions produce bands at 430, 700 and 830 nm [11, 23].

The optical spectrum of Ni-doped glass before irradiation reveals the strong UV absorption due to trace iron impurity together with sharp and intense band at 430 nm, a small peak at about 720 nm and broad band centered at 850 nm. All these visible spectral bands are related to dominance of octahedral coordinated Ni^{2+} ions. Gamma irradiation produces minor variations without extra induced bands.

(h) **Copper-doped glass**

Copper can be present in glasses as the divalent Cu^{2+} (d^9) ions [11, 23]. The monovalent Cu^+ (d^{10}) ions can be prepared under some circumstances of reducing condition beside metallic Cu^0 present as colloidal suspension in the copper ruby glass.

The Cu^+ ion having a d^{10} configuration will not impart color to the glass but they show UV absorption. The d^9 configuration of the cupric ions (Cu^{2+}) impart normally a

single very broad band which at high concentration of copper ions can show splitting to several component peaks as mentioned by Paul [34].

Experimental spectrum of Cu-doped glasses reveal sharp UV absorption bands with distinct peaks which are related to iron impurities and the single broad visible-near IR region centered at about 820 nm is related to distorted octahedral Cu^{2+} ions. Gamma irradiation reveals stability of the spectral features except the decrease in intensity of the visible near IR broad band with parallel behavior to that before irradiation. This trend confirms previous observation of the shielding effect of Cu-containing glasses reached by some authors [20, 21].

4.1.3 Interpretation of the FTIR Spectra of un-doped and 3d TM Ions-Doped Bismuth Phosphate Glasses

The FTIR spectra can be realized and interpreted on the following basis [35–39]:

- (a) The IR spectral bands are identified to be extended from the wavenumber ranges $400\text{--}1600\text{ cm}^{-1}$ and containing the main vibrational modes due to main phosphate groups (70 mol% P_2O_5). The bismuth ions present in (30 mol%) are obviously represented interfering in the far-IR broad band at about 494 cm^{-1} and possibly another IR vibrations overlapped by the mode extending from about $800\text{--}1550\text{ cm}^{-1}$ connected with phosphate network.
- (b) Many glass scientists [35, 36] have reached to the close resemblance of IR vibrations modes of various phosphate glasses and their crystalline analogues.
- (c) The deconvoluted peaks at about $540\text{--}460\text{ cm}^{-1}$ can be related to both bending or harmonic vibration of P-O-P bonds or PO_2 modes beside sharing of vibrations of Bi-O-Bi, Bi-O in BiO_6 octahedra [37–39].
- (d) The deconvoluted peaks at $760\text{--}650\text{ cm}^{-1}$ can be attributed to the symmetric vibrations of P-O-P groups.
- (e) The distinct peak at $910\text{--}890\text{ cm}^{-1}$ is related to asymmetric stretching vibrations of P-O-P groups and also to metaphosphate groups.
- (f) The peak at $1060\text{--}990\text{ cm}^{-1}$ can be related to asymmetric stretching vibration of P-O-P groups.
- (g) The deconvoluted peaks at $1230\text{--}1160\text{ cm}^{-1}$ can be related to asymmetric vibrations of metaphosphate chains (PO_2^- units), stretching vibrations of doubly bonded oxygen vibration (P=O).
- (h) The peaks at $1320\text{--}1280\text{ cm}^{-1}$ are characteristic for vibrations of nonbridging PO_2 groups.
- (i) The small peak at about 1640 cm^{-1} is attributed to vibrations of water and/or OH groups.
- (j) The small broad band centered at about 3450 cm^{-1} can be related to vibrations of H_2O , OH, POH and the

low intensity of this broad band is related to presence of Bi_2O_3 in (30 mol %) which reduces the ability to absorb surface water vapor.

5 Conclusion

Glasses of the basic composition (Bi_2O_3 30 mol%– P_2O_5 70 mol%) with additional dopants 3d TM oxides (0.2 wt%) have been prepared and characterized for their optical and FTIR spectra before and after gamma irradiation (dose 8 Mrad). Optical spectra show two strong UV bands related to trace iron impurity beside a small peak due to absorption of Bi^{3+} ions while TM ions-doped glasses reveal characteristic bands due mainly to the lower valence or octahedral coordination. Some of the transition metal ions are observed to show shielding behavior towards gamma irradiation.

Detailed optical spectra due to 3d TM ions are discussed in relation to the dominance of lower valence or octahedral coordination and possibility of photochemical reactions during the irradiation process. FTIR spectra show characteristic vibrational modes due to phosphate groups and the sharing of Bi-O vibrations.

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