

Reducing Power of Phosphate Matrix in Binary Barium Phosphate Glasses Doped with 3d Transition Metals and Effects of Gamma Radiation

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Abstract Spectroscopic characterization was performed for base and first row transition metal ions (3d TM) doped barium metaphosphate glasses. The procedure was conducted using FTIR and optical spectral measurements before and after 8 M rad gamma irradiation. Electronic spectra show distinct UV absorption with a peak around 230 nm in nearly all samples correlated with trace iron ions present as an impurity within the chemicals used for the preparation of the glasses. 3d TM ions-doped samples exhibit additional characteristic bands mainly in the visible due to each respective TM ion. Such optical spectra indicate and support the assumption that the host phosphate glass generally promotes the reduced state or octahedral coordination of the TM ions to a measurable extent. Gamma irradiation produces mostly an extension of the UV spectra and this effect is correlated with the assumption of photochemical reactions of the trace iron ions impurities during the irradiation process in which some ferrous ions capture positive holes and are transformed to additional ferric ions causing the extension.

FTIR absorption spectra reveal vibrational bands due mainly to metaphosphate groups and the P-O-P mode while TM ions doped glasses show no distinct variations due to the stability of the phosphate network containing high content of heavy Ba²⁺ ions and the presence of TM ions in low doping percent.

Keywords Barium phosphate glass · 3d TMs · Optical FTIR spectra · Gamma irradiation

1 Introduction

Renewed interest in understanding the properties of phosphate glasses in relation to their constitutional structure has extended their applications. Phosphate glasses are generally known to possess high thermal expansion coefficients and low preparation temperatures and some compositions are therefore suitable as sealing candidates [1–3]. The high transparency for ultraviolet light (UV) of phosphate glasses together with the ability to incorporate a high content of rare earth and transition metal ions suggest high power laser applications especially when mixed with fluoride ions [4]. The reasonable chemical stability and low processing temperature of iron phosphate and lead iron phosphate glasses have resulted in claims for their development as nuclear waste hosts [5]. Various phosphate glasses and glass-ceramics have been recommended for medical applications [6, 7].

The addition of modifying oxide (alkali or alkaline earth oxide) to P₂O₅ results in the creation of non-bridging oxygens at the expense of bridging oxygens. The metaphosphate glasses (with 0.50 ratio of modifier oxide) have a network based entirely on Q² tetrahedra that form chains and rings. The chains and rings are linked by more ionic

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bonds between various metal cations and the non-bridging oxygens [2].

Some phosphate glasses with divalent oxides (such as MgO or ZnO) seem to exhibit anomalous behavior or unusual discontinuities in composition-property dependence (e.g. refractive index and molar volume) at the metaphosphate composition which was related to the coordination change of the modifying cation [8]; Kanazwo [9] has proposed this anomaly in the depolymerization of the phosphate network.

Glasses containing 3d transition metals (TMs) possess valuable physical properties due to the presence of these TMs in more than one valence or coordination state [10, 11]. The percent of each valence varies with the number of electrons in the 3d subshell, type or composition of the host glass and condition of melting.

Some glass scientists have studied collective 3d transition metal ions in various phosphate glasses [12–16], and have reached the conclusion that the TM ions generally exist in their low valence state or octahedral coordination. They have concluded that the composition of the host glass affects the valency of the transition metal ion. They also note that the phosphate glasses are a better acceptor of O^{2-} than silicate and borate glasses and hence the oxide reduction equilibrium is shifted towards the reduced state [12].

Gamma irradiation has been observed to produce induced optical (UV/vis.) absorption bands upon irradiation of undoped alkali phosphate glasses [13–16]. The presence of heavy metal oxides (such as PbO, Bi_2O_3) causes a noticeable retardation of the effects of gamma irradiation and also the incorporation of some TM ions (e.g. V^{5+} , Cu^{2+}) shows the same shielding behavior or stability of glasses after irradiation.

A recent review on phosphate and fluoride phosphate optical glasses including their properties, structure and applications by Ehrt [17] has included strontium phosphate and others phosphate glasses together with the effect of different radiation sources for its importance in optics and optoelectronics.

The objective of this study is to prepare some barium metaphosphate glasses of the basic composition (50 mol% BaO-50 mol% P_2O_5) and containing 0.2 % of one of the 3d transition metal oxides (TiO_2 , V_2O_5 , Cr_2O_3 , MnO_2 , Fe_2O_3 , CoO, NiO, CuO). Collective UV/vis and IR absorption spectra of the prepared glasses were measured before and after gamma irradiation with a dose of 8 Mrad (8×10^4 Gy). This work is expected to give detailed spectral data justifying the stable valence states of the different 3d TMs in this host glass and also the effects of gamma irradiation on the UV/vis. absorption spectra and on the vibrational bands in relation to their structural arrangement. These objectives are most important for optical glass compositions in nuclear and various optical applications.

2 Experimental Details

The studied barium phosphate glasses with nominal composition (50 mol.% BaO, 50 mol.% P_2O_5) were prepared from analytical pure grade chemicals. The materials used included, ammonium dihydrogen phosphate for P_2O_5 , and heavy barium carbonate for BaO, and the first row 3d transition metal oxides were introduced separately within the batches as an additional 0.2%. Weighed batches were melted at 1100 °C for 2 hours under ordinary atmospheric condition in platinum 2%Rh crucibles. Molten batches were rotated at fixed intervals to reach complete mixing and homogeneity of the melts. Melts were transferred into warmed stainless steel molds of the required dimensions. The glasses were immediately transferred to an annealing muffle at 300 °C which was left to cool after 1 hour to room temperature. Ultraviolet and visible (UV/vis.) optical absorption spectra were immediately measured for polished samples of 2 ± 0.01 mm thickness before and after gamma irradiation using a double beam spectrophotometer (JASCO V-570) in the spectral range from 190 to 1100 nm. A computerized FTIR spectrometer (type, Nicolet iS10, USA) was employed to measure FTIR spectra in the spectral range 4000-400 cm^{-1} . Prepared samples in the powdered form were mixed with KBr powder in the ratio 1:100 mg and subjected to a constant load of 5 tons/ cm^2 to produce clear homogeneous discs. The infrared absorption spectra were measured for un-irradiated and irradiated samples after preparing the desired discs. An Indian ^{60}Co gamma cell (2000 Ci) was used as a γ -ray source with a dose rate of 150 rad/s at a constant temperature of 30 °C. Glass samples were subjected to a final gamma dose of 8×10^4 Gy (8M rad).

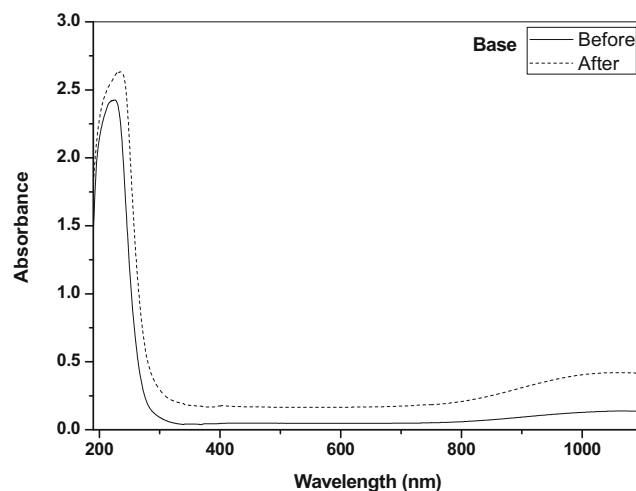


Fig. 1 Optical absorption spectra of base undoped barium phosphate glass before and after gamma irradiation

3 Results and Discussion

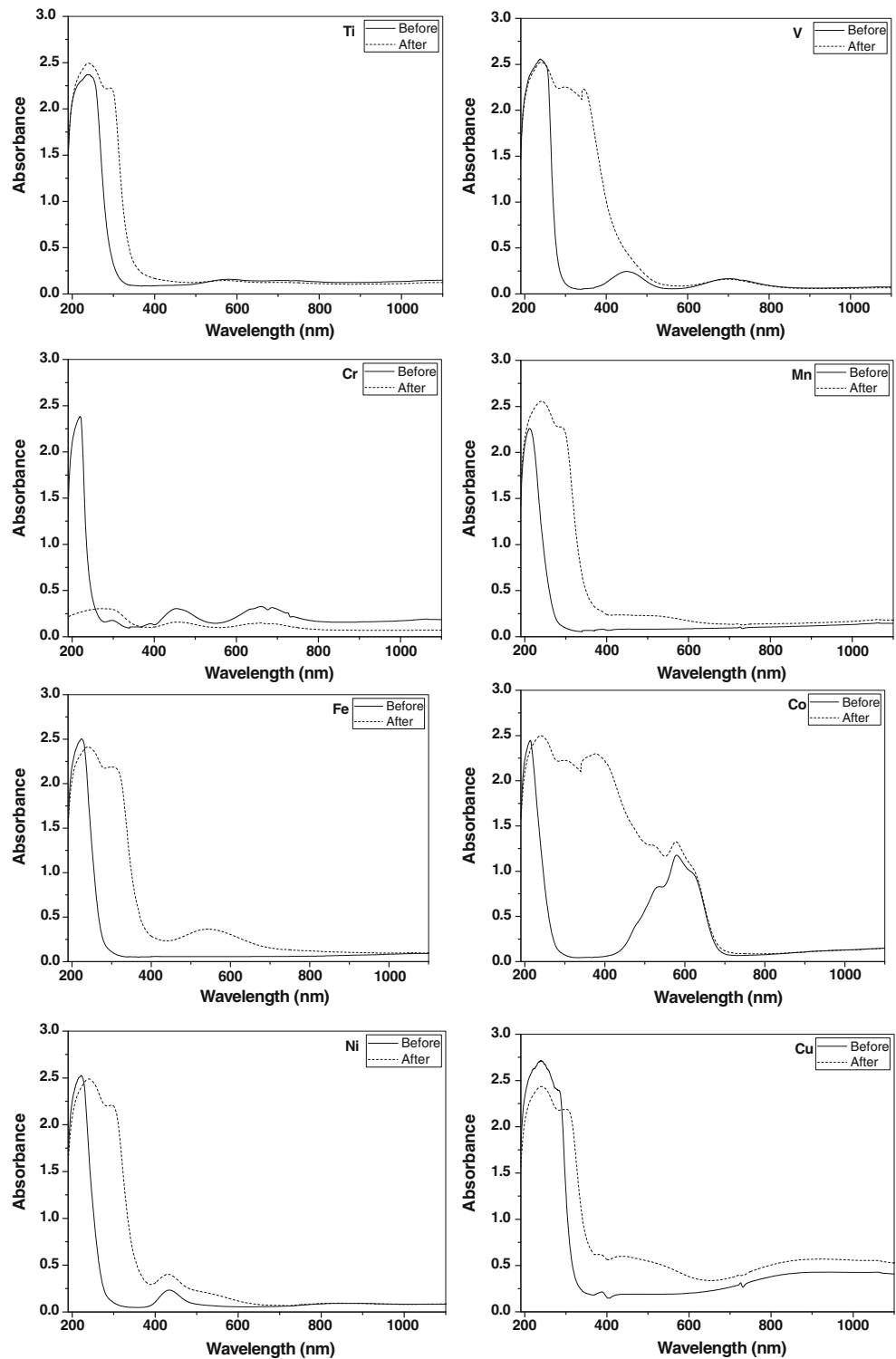
3.1 Optical Absorption Spectra of the Studied Undoped and 3d TM-Doped Glasses

Figure 1 shows the (UV/Vis) optical absorption spectra of the parent barium phosphate glass before and after gamma

irradiation. The spectrum displays distinct UV absorption with a peak at about 225 nm with no further absorption to the end of measurement at 1100 nm. After gamma irradiation, the intensity of the UV and visible absorption slightly increases in intensity without any induced visible bands.

Figure 2 shows the UV/vis absorption spectra of the studied 3d TMs-doped glasses before and after gamma

Fig. 2 Optical absorption spectra of base TMs-doped barium phosphate glass before and after gamma irradiation



irradiation. The detailed spectral results are summarized as follows:

1. The optical spectra of the glasses before and after irradiation show somewhat broader strong UV absorption with a peak at about 240 nm.
2. Characteristic peaks corresponding to absorption of TM dopants appear in the visible region.
3. After gamma irradiation, the overall spectra reveal broadening of the UV absorption with the resolution of an extra UV peak.

3.2 FTIR Absorption Spectra of the Studied Glasses Before and After Irradiation

Figure 3 illustrates the FTIR absorption of the studied glasses. The undoped barium phosphate glass shows the presence of a broad and intense far-IR band with multiple peaks, a medium broad band with a peak at 762 cm^{-1} , a very broad band extending from about 800 cm^{-1} to about 1120 cm^{-1} , an intense broad band centered at 1287 cm^{-1} , a small peak at about 1640 cm^{-1} followed by five small peaks at about 2320, 2340, 2430, 2850 and 2930 cm^{-1} .

All the FTIR spectra of the various 3d TM ions-doped glasses are very similar to the IR spectrum of the undoped glass, specifically the detailed number and position of the characteristic IR vibrational bands. Gamma irradiation causes no variations of the IR spectral vibrational bands, specifically their number and position.

3.3 Interpretation of the Strong UV Spectrum of the Undoped Barium Phosphate Glass

It has been recognized that various undoped phosphate glasses exhibit strong UV absorption due to the presence of

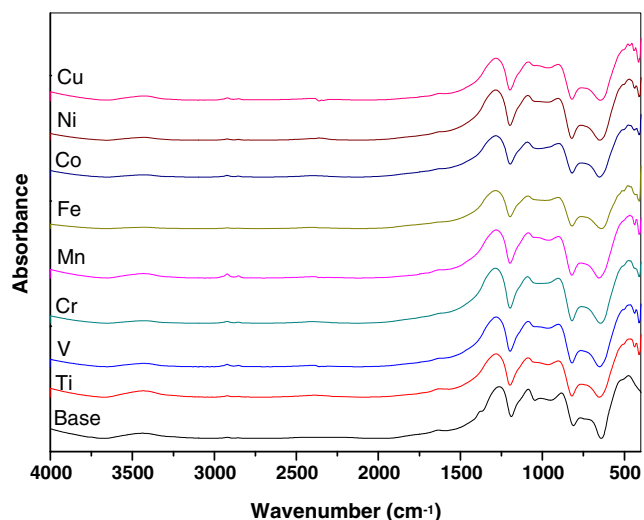


Fig. 3 FTIR absorption spectra of the studied glasses before irradiation

unavoidable trace iron impurities (mainly Fe^{3+} ions) contaminated within the chemicals used for the preparation of phosphate glasses [13–17].

Duffy [18, 19] has reviewed and classified charge transfer UV spectra in various glasses. He has assumed that certain transition metal ions (e.g. Fe^{3+} , Cr^{6+}) exhibit strong charge transfer UV spectra even if present in the ppm level. He has related this charge transfer UV spectra to originate from an electron transfer mechanism involving the transition of an electron from the orbital of a coordinated oxygen to an orbital of the metal ion.

We can therefore assume that the UV absorption band at 215–225 nm identified in the studied glasses can be related to the presence of traces impurities of iron (Fe^{3+} ions).

3.4 Interpretation of the Optical Absorption of 3d TM Ions-Doped Glasses

The detailed assignments of the absorption spectra of the 3d TMs ions-doped glasses are summarized as follows:

a. Titanium-doped glass

This glass exhibits an additional broad visible curvature centered at 560 nm. This new identified visible absorption at 560 nm is related to the presence of Ti^{3+} ions because of the reducing action of the host barium phosphate glass. The Ti^{3+} ion belongs to the $3d^1$ configuration and hence exhibits a single visible band around 500–580 nm [10, 11, 20].

b. Vanadium-doped glass

This V-doped glass reveals two additional broad visible bands centered at 450 and 700 nm related to the presence of lower valencies of vanadium namely V^{3+} and V^{4+} ions which are known to exhibit characteristic visible bands. The first band at 450 nm can be related to tetravalent vanadium ions and the second band at 700 nm is due to absorption of trivalent vanadium ions [10, 11, 21].

c. Chromium-doped glass

This Cr-doped glass exhibits two additional broad visible bands, the first centered at 450 nm and the other band is split into three peaks at about 630, 670 and 690 nm. The two identified broad visible bands are connected with the presence of the lower valence of trivalent chromium ions in high content, in the form of octahedrally coordinated Cr^{3+} ions [10, 11, 22].

d. Manganese-doped glass

This Mn-doped glass reveals no extra visible bands but only the strong UV band due to trace Fe^{3+} ions present as an impurity which is the only one identified. It can be assumed that the phosphate glass brings the reduction of added manganese ions as dopants (0.2% MnO_2) to the divalent manganese (Mn^{2+} ions) and the

expected visible absorption bands from the divalent Mn^{2+} ions are not clearly identified due to their forbidden nature and also they cannot be clearly identified unless the concentration of the manganese ions exceeds 5% as mentioned by some authors [10, 11] while the added dopant MnO_2 in this study is (0.2%).

e. Iron-doped glass

The spectrum of this Fe-doped glass resembles completely the spectrum of the undoped glass. This confirms our assumption that the identified UV absorption bands in all the studied glasses have originated from traces of ferric ions present as impurities.

f. Cobalt-doped glass

The spectrum of this Co-doped glass shows an additional broad visible band extending from about 420 to 700 nm with three distinct peaks at 530, 580 and 622 nm. These distinct visible peaks are related to the existence of both octahedral and tetrahedral coordination of Co^{2+} ions. This behavior is due to the close stabilization energies for the two coordination states of divalent cobalt ions as has been mentioned by several authors [10, 11, 16].

g. Nickel-doped glass

This Ni-doped glass exhibits a spectrum with an additional medium band centered at 435 nm. This band is correlated with the presence of stable octahedral divalent nickel ions [10, 11, 14].

h. Copper-doped glass

This Cu-doped glass reveals an extension of the UV absorption to two strong peaks at 240 and 280 nm besides two small kinks at 380 and 420 nm and a very broad visible curvature is observed centered at about 800 nm. The extended UV-near visible peaks are related to Fe^{3+} ions due to additional impurity of ferric ions with the dopant 0.2% CuO. The very broad visible-near IR curvature is correlated with distorted octahedral Cu^{2+} ions [10, 11].

3.5 Interpretation of the Effect of Gamma Irradiation on the Optical Spectra

It is recognized that radiation can induce numerous changes in the physical and chemical properties of glass and one of the most obvious properties is visible coloration (or darkening) and for this reason the produced defect centers causing this coloration are often referred to as “color centers” [17, 22, 23]. When ionizing radiation such as gamma rays or UV radiation impinges on the glass, electrons and positive holes are generated and react with intrinsic defects (e.g. non-bridging oxygens, flaws, trace impurities) already present in the glass before irradiation. Glasses are known to be materials of non-periodic nature and contain vacancies, non-bridging oxygens and trace impurities which are ready to trap

electrons or positive holes. When a glass contains transition metal ions, these TM ions compete for released electrons and positive holes and the result is the conversion of the valencies of the TM ions. Also, the presence of some heavy metal oxides (e.g. PbO , Bi_2O_3 , BaO , CdO) is observed to cause some shielding effects towards gamma irradiation [20].

Experimental data indicate that gamma irradiation produces mainly a marked growth or extension of the UV absorption in undoped and most TMs-doped glasses and with the two samples of Fe-doped and Cu-doped an extra induced visible band at about 550 nm. Such induced changes can be explained by assuming that trace iron impurities contain ferrous ions due to the reducing effect of phosphate glass. Upon gamma irradiation, some ferrous (Fe^{2+}) ions are assumed to capture by photochemical reactions positive holes and are transformed to additional ferric (Fe^{3+}) ions which have their main absorption in the region 200–240 nm and thus the observed extension of UV is identified. The generation of an induced visible band at 550 nm as mentioned in two samples can be correlated with the formation of nonbridging oxygen hole centers (NBOHC) or phosphorus oxygen hole centers (POHC) as suggested by Bishay [23], Friebele [24] and Moncke and Ehrh [13].

3.6 Interpretation of the FTIR Spectra of the Studied Undoped and TMs Ions-Doped Barium Phosphate Glass

The observed IR absorption spectra can be explained as follows:

- The main IR spectral features are observed to be extended from the wavenumber range 400 cm^{-1} to about 1600 cm^{-1} representing the vibrations due to the phosphate network mainly from the metaphosphate groups as expected from the basic composition of the host glass (50%BaO-50% P_2O_5). The barium cations are accepted to occupy interstitial positions as modifiers.
- Various authors [25–30] have identified the close resemblance of vibrations of phosphate glasses and their analogous crystalline phosphates.
- The far IR band with several peaks at $424\text{--}509\text{ cm}^{-1}$ can be related to the bending or harmonic vibrations of P-O-P bands or PO_2 modes.
- The medium band with the peak at 762 cm^{-1} may be attributed to the symmetric vibrations of P-O-P groups.
- The distinct peak at 904 cm^{-1} is related to vibrations of metaphosphate groups.
- The peak at 1089 cm^{-1} can be related to asymmetric stretching of P-O-P groups.
- The high intense band with a peak at 1287 cm^{-1} can be related to asymmetric stretching vibrations of metaphosphate (PO_2) units.

- h. The peak at 1640 cm^{-1} is related to vibrations of water, OH groups.
- i. The small peaks within the range $2320\text{--}2980\text{ cm}^{-1}$ are related to molecular water, OH, or POH vibrations and the same assignment is given to the broad near-IR band at 3430 cm^{-1} due to the ability of phosphate glass powder to absorb moisture during the preparation of the KBr discs.

4 Conclusion

Optical absorption spectra of the studied undoped and 3d doped barium phosphate glasses show distinct ultraviolet absorption due to trace iron impurities (Fe^{3+} ions) besides characteristic visible bands due to transition metal ions mostly in their low valence states or octahedral coordination.

Gamma irradiation is identified to concentrate its effect mainly on the UV absorption which extends to reach the visible region with the resolution of extra UV bands. These effects are attributed to photochemical effects on some Fe^{2+} ions, due to the reducing action of the host glass photooxidizing to Fe^{3+} ions. Some samples reveal an induced visible band which can be related to non-bridging oxygen hole centers or phosphorus oxygen hole centers.

FTIR spectra of the prepared glasses show repetitive IR vibrational bands consisting mainly of metaphosphate groups and the TM ions introduced in low dopant level (0.2%) cause no obvious changes in the number or position of the vibrational bands. The stability of the network structure of the studied phosphate glasses can be related to the presence of 50 mol% of heavy metal oxide (BaO).

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