

Research Article

Optical and FT Infrared Absorption Spectra of 3d Transition Metal Ions Doped in NaF-CaF₂-B₂O₃ Glass and Effects of Gamma Irradiation

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Combined optical and FTIR spectroscopy has been employed to investigate the undoped NaF-CaF₂-B₂O₃ glass together with samples containing 0.2% dopant of 3d TM ions before and after gamma irradiation. The optical spectrum of the undoped glass reveals strong UV absorption with two peaks which are related to unavoidable trace iron impurity within the raw materials. Upon gamma irradiation, an induced visible broad band centered at 500 nm is resolved and is related to B-O hole center or nonbridging oxygen hole center. TMs-doped samples exhibit characteristic absorption due to each respective TM ion but with faint colors. Gamma irradiation of TMs-doped samples reveals the same induced visible band at 500–510 nm in most samples except CuO and Cr₂O₃-doped glasses. Infrared absorption spectra reveal characteristic vibrational bands due to triangular and tetrahedral borate groups. The introduction of NaF and CaF₂ modifies the borate network forming BO₃F tetrahedra. The introduction of 3d TMs as dopants did not make any obvious changes in the FTIR spectra due to their low content (0.2%). Gamma irradiation causes only minor variations in the intensities of the characteristic IR borate bands while the bands at about 1640 cm⁻¹ and 3450 cm⁻¹ reveal distinct growth in most samples.

1. Introduction

Borate glasses belong to a valuable and interesting system which finds applications for optical, thermal, electrical, and biological purposes [1–3]. The basic building oxide for borate glass is B₂O₃ which consists of triangular BO₃ units arranged mostly as boroxol rings (B₃O₆) [4]. Upon the addition of an alkali oxide, alkaline earth oxide, or heavy metal oxide (e.g., PbO, Bi₂O₃, and Sb₂O₃) successive parts of BO₃ groups are changed to BO₄ groups until certain limit after which the excess additions of the mentioned oxides form nonbridging oxygens. Borate glasses unlike silicate and phosphate glasses possess rich chemistry where different structural groups or super structural units can be formed. The infrared spectra of structural vibrational groups belonging to BO₃ or BO₄ units have varying wavenumber positions. The BO₄ groups are vibrating within the range 800–1200 cm⁻¹ while the BO₃

(B₂O⁻) groups are within the wavenumber 1200–1600 cm⁻¹ [4].

Some glass scientists have prepared and characterized borate glasses containing alkali, alkaline earth, and divalent halides instead of the respective oxides [5–8]. These types of borate glasses containing halide anions (e.g., F⁻) possess interesting optical and anionic conduction properties. These authors concluded that these glasses mainly contain BO₃, BO₂F triangles, BO₄, and BOF₃ tetrahedra. Formation of BO₂F triangles is, however, ruled out. Doweidar et al. [8] have utilized FTIR spectroscopy to find out the structure of binary B₂O₃-CaF₂ glasses. They have proposed that CaF₂ partially modifies the borate network forming Ca⁺²_{1/2}[BO_{3/2}F]⁻ units and the rest of CaF₂ is assumed to build an amorphous network formed of CaF₄ tetrahedra. The IR spectra of the CaF₂-B₂O₃ glasses are found to be similar to that usually identified from the IR spectra of alkali and alkaline earth

borate glasses. There are two main separate strong and broad absorption bands in the regions 800–1200 and 1200–1800 cm⁻¹ in addition to a small band around 700 cm⁻¹ and there is no change in the band centers with composition of glass. Doweidar et al. [8] have concluded that the B₂O₃ is modified through the formation of BO₄ and BOF₃ tetrahedra with CaF₂ as there is no modifier oxide. They have further assumed that [BO_{3/2}F]⁻ distorted tetrahedra are suggested to be the single or the most probably formed oxyfluoroborate species. The absorption in the region 800–1200 cm⁻¹ is related to the suggested formed BO₃F (B₄).

It is accepted that ionizing irradiation causes obvious changes in the optical spectra of undoped and 3d transition metals-doped glasses through the capturing of released pairs of electrons and positive holes and the formation of induced defects which may give rise to new optical bands [9, 10]. The authors have shared in extensive spectral studies on the spectral properties of 3d TM ion doped in various oxide glasses (borate, silicate, and phosphate) which indicate the competition of TM ions with intrinsic defects already present in glasses and can change their valences through photochemical reactions [11, 12]. These studies have indicated that some transition metal ions show shielding behavior towards gamma irradiation and this results in the maintenance of the absorption curves revealing no changes.

In the course of the present work, combined optical and FT infrared spectroscopic measurements have been employed to investigate the states of 3d transition metal ions in the host NaF-CaF₂-B₂O₃ glass and identify the structural building units involved and the effects of gamma irradiation on the studied combined spectral properties. This study will be expected to identify the induced defects generated through the irradiation process. Also, the work aims to compare the difference of introducing fluoride anions instead of oxygens on both the optical and FT infrared spectral analyses of the doped glasses.

2. Experimental Details

2.1. Preparation of the Glasses. The base undoped glass of the composition (wt%) B₂O₃ 80%, NaF 15%, CaF₂ 5% together with samples of the same basic composition but containing 0.2% of one of the 3d transition metal oxides (namely, TiO₂ → CuO) was prepared from pure chemicals of boric acid, NaF, CaF₂, and 3d TM oxides: TiO₂, V₂O₅, Cr₂O₃, MnO₂, Fe₂O₃, CoO, NiO, and CuO.

The weighed batches were mixed thoroughly and melted in platinum 2% Rh crucibles at 1100°C for one and half hours in an electric heated SiC rods furnace (Vecstar, F₂, UK). The platinum crucibles containing the melts were rotated several times to reach acceptable homogeneity. The melts were poured within warmed stainless steel molds of the required dimensions. The prepared samples were immediately transferred to an annealing muffle furnace regulated at 400°C. The muffle was switched off after 1 hour and left to cool to room temperature at rate of 25°C/h.

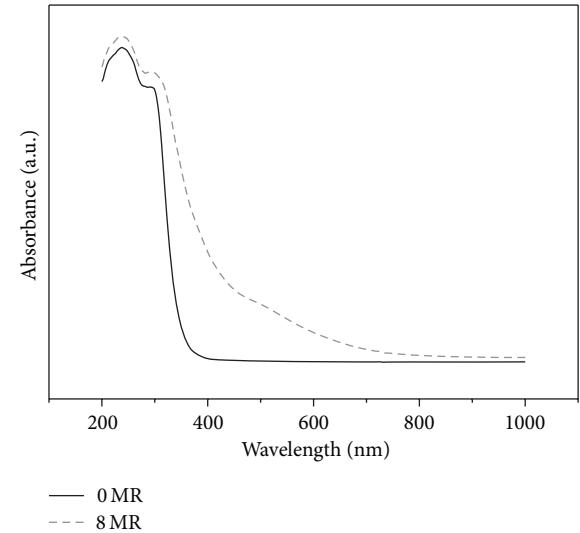


FIGURE 1: Optical absorption spectra of undoped fluoroborate glass before and after gamma irradiation (8 Mrad).

2.2. Optical Absorption Spectral Measurements. The optical absorption spectra (UV-visible) of polished samples (thickness 2 mm ± 0.1 mm) were recorded at room temperature before and after gamma irradiation using a recording spectrophotometer (type Jasco Corp., V-570, Rel-00, Japan) concerning the range 200–1000 nm.

2.3. Infrared Absorption Spectral Measurements. The FTIR spectra of the glasses were measured by adopting the KBr disc technique. The measurements were done by a Fourier transform computerized IR spectrometer type (Jasco, FT/IR-4600, Japan) in the wavenumber range 4000–400 cm⁻¹. The samples were examined as fine powders which were mixed with pulverized KBr in the ratio 1:100 glass powder to KBr, respectively. The weighed mixtures were subjected to a pressure of 5 tons/cm² to produce clear homogenous discs. The FTIR measurements were carried out immediately after preparing the discs and the same measurements were repeated after gamma irradiation.

2.4. Gamma Irradiation Facility. A ⁶⁰Co gamma cell (2000 Ci) was used as a gamma-ray source with a dose rate of 1.5 Gy/s (150 rad/s) at room temperature (30°C). The glass samples were placed in the gamma cell in the manner that each sample was subjected to the same gamma dose. By using a Fricke dosimeter the absorbed dose was measured in water, rather than in terms of dose in glass. No cavity theory correction was made. Each glass was subjected to a gamma dose of 8 × 10⁴ Gy (= 8 Mrad).

3. Results

3.1. Optical (UV-Visible) Absorption Spectra of the Studied Glasses. Figure 1 illustrates the optical UV-visible absorption spectrum before and after irradiation of the base undoped

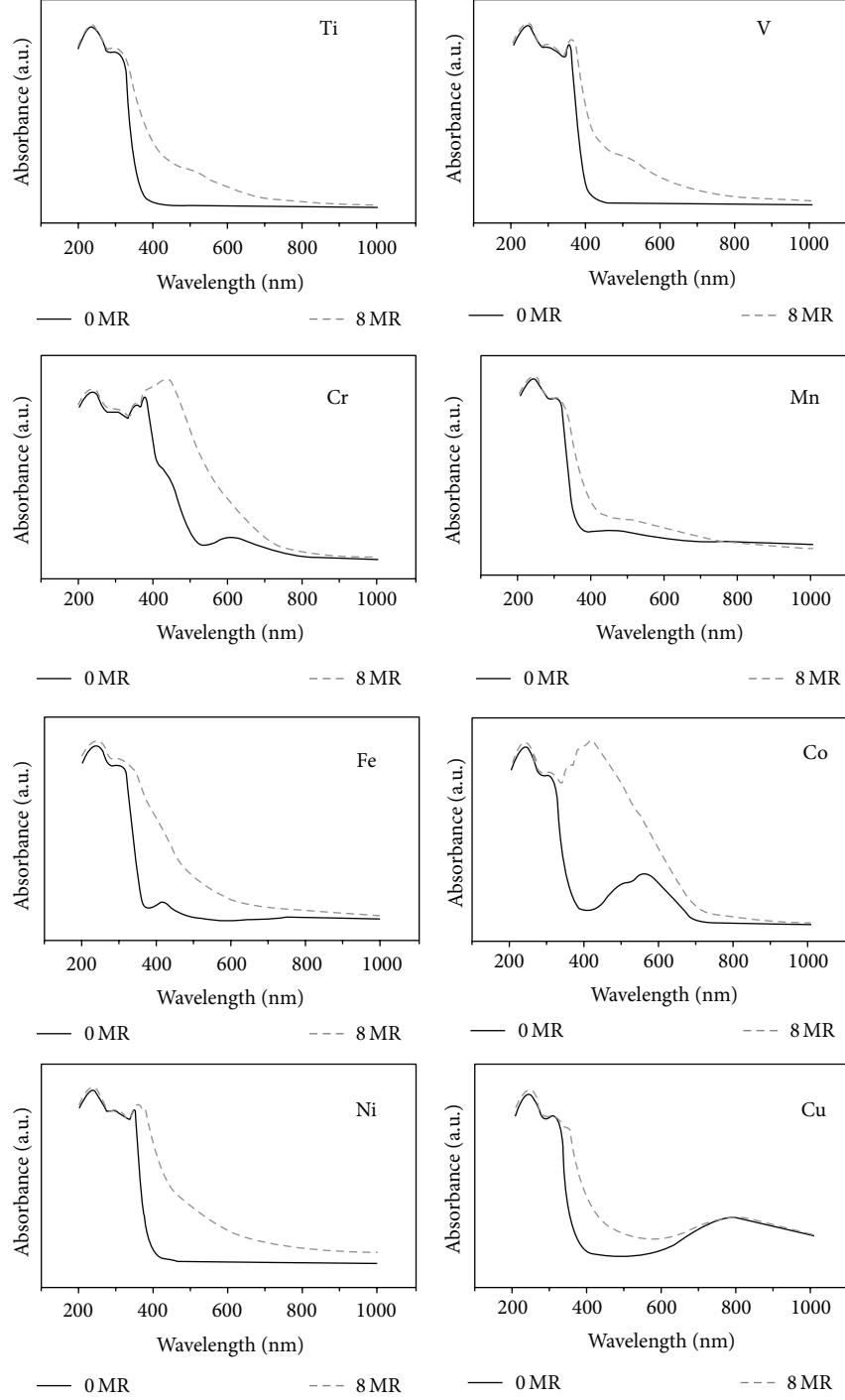


FIGURE 2: Optical absorption spectra of 3d TMs-doped fluoroborate glasses before and after gamma irradiation.

$\text{NaF-CaF}_2\text{-B}_2\text{O}_3$ glass. The spectrum reveals a strong UV broad absorption extending from 200 to about 350 nm and showing two distinct peaks at 236 and 292 nm and with no visible absorption bands. The base glass after irradiation shows an extra induced visible band centered at about 500 nm.

Figure 2 reveals the optical absorption spectra of 3d TM ions-doped glasses before and after irradiation. The spectra

show variable optical absorption with the type of 3d TM ions and the spectral data can be summarized as follows.

3.1.1. Titanium-Doped Glasses. This TiO_2 -doped glass reveals before irradiation a spectrum similar to that observed from the undoped glass and showing strong and broad UV absorption with two distinct peaks at 238 and 293 nm. Upon gamma

irradiation, the spectrum shows an extra induced visible broad band centered at 508 nm.

3.1.2. Vanadium-Doped Glass. This V_2O_5 -doped glass shows before irradiation a spectrum consisting of a strong and broad UV absorption revealing three distinct peaks at 238, 298, and 349 nm and no visible absorption bands are identified. The irradiated glass reveals a spectrum showing an extra visible broad band centered at 505 nm.

3.1.3. Chromium-Doped Glass. This Cr_2O_3 -doped glass reveals before irradiation a connected UV-visible absorption spectrum consisting of strong broad UV absorption with four peaks at 234, 304, 349, and 378 nm and attached with a broad band at 431 nm and with finally a broad and medium visible band centered at 615 nm. Upon gamma irradiation, the spectrum reveals the persistence of the UV-visible bands until that at 433 nm and no other induced bands are observed.

3.1.4. Manganese-Doped Glass. This MnO_2 -doped glass shows before irradiation a spectrum with the same strong and broad UV absorption with two peaks at 242 and 299 nm followed by a broad visible band centered at 444 nm. The irradiated glass reveals an additive new visible broad band centered at 510 nm.

3.1.5. Iron-Doped Glass. This Fe_2O_3 -doped glass reveals before irradiation the same strong and broad UV absorption with two peaks at 239 and 295 nm followed by a medium broad visible band centered at 415 nm. The irradiated sample reveals two UV bands at 234 and 295 nm followed by two induced visible bands at 406 and 506 nm.

3.1.6. Cobalt-Doped Glass. This CoO -doped glass shows before irradiation a spectrum with the same strong and broad UV absorption as the undoped glass with two distinct peaks at 236 and 295 nm. This is followed by a very broad visible absorption extending from 400 to 700 nm showing two peaks at 491 and 556 nm and with a further small peak at 725 nm. The irradiated glass shows four UV bands at 234, 297, 359, and 395 nm followed by two visible bands at 415 and 543 nm.

3.1.7. Nickel-Doped Glass. This NiO -doped glass shows before irradiation strong and broad UV absorption with three distinct peaks at 241, 298, and 347 nm followed by a small peak at about 435 nm. This glass after irradiation shows four UV peaks at 238, 297, 357, and 390 nm followed by an induced broad visible band centered at 500 nm.

3.1.8. Copper-Doped Glass. This CuO -doped glass reveals before irradiation the same strong and wide UV absorption with two distinct peaks at 239 and 296 nm followed by a very broad medium band centered at 794 nm. Upon gamma irradiation, the glass shows an additional UV band at 340 nm and the other bands remain as before irradiation.

3.2. Infrared Absorption Spectra of the Studied Glasses. Figure 3 illustrates the FTIR spectra of the undoped and 3d TMs-doped $NaF-CaF_2$ borate glasses which reveal almost repetitive spectral vibrational bands with some limited variations. The IR spectrum of the base undoped glass shows the following spectral features:

- (a) a small band is observed at about 480 cm^{-1} ;
- (b) a strong sharp band is identified at about 698 cm^{-1} ;
- (c) a first strong broad with two identified peaks at 910 and 1040 cm^{-1} ;
- (d) a second strong broad band with two distinct peaks identified at 1230 and 1408 cm^{-1} ;
- (e) two small curvature are observed at about 1450 and 1650 cm^{-1} ;
- (f) two small peaks are observed at about 2830 and 2907 cm^{-1} ;
- (g) a broad near IR medium band centered at 3430 cm^{-1} is observed.

Figure 3 also reveals that all the glasses containing 3d TM ions exhibit the same fundamental and characteristic IR absorption bands observed in the spectrum of the undoped glass. Only some minor changes of the intensities of some bands are observed but keeping the most distinctive four bands around 700 cm^{-1} and the two broad bands extending from 800 to 1200 cm^{-1} and from 1200 to 1600 cm^{-1} and the final broad near IR band centered around 3430 cm^{-1} .

3.3. Infrared Absorption Spectra after Gamma Irradiation. Figure 4 illustrates the FTIR spectra of the studied glasses after being subjected to gamma irradiation with a dose of 8 Mrad. Inspection of the IR spectral curves indicates that the main characteristic bands due to triangular and tetrahedral borate remain almost unaffected except by minor or limited changes of the intensities of some bands. The specific bands at 1635 – 1645 cm^{-1} and 3450 – 3460 cm^{-1} show distinct responses with irradiation becoming more prominent in most cases.

4. Discussion

4.1. Interpretation of the UV Absorption Spectra from Undoped $NaF-CaF_2-B_2O_3$ Glass. Duffy [13] has recognized and classified differently originated ultraviolet absorption in various glasses. He assumed that some transition metal ions (e.g., Fe^{3+} , Cr^{6+} , ...) when present in doping level in glasses exhibit characteristic charge transfer ultraviolet absorption spectral bands even if present in the ppm level. Such metal ions owe their strong ultraviolet spectra in glasses to an electron transfer mechanism. But certain other metal ions including Ce^{3+} , Tb^{3+} , and U^{4+} as well as $d^{10}\text{ S}^2$ ions (such as Pb^{2+} and Bi^{3+}) absorb radiation through electronic transitions involving orbitals essentially of the metal ion only, and the name “Rydberg” has been suggested for such spectra to distinguish them for the charge transfer UV spectra.

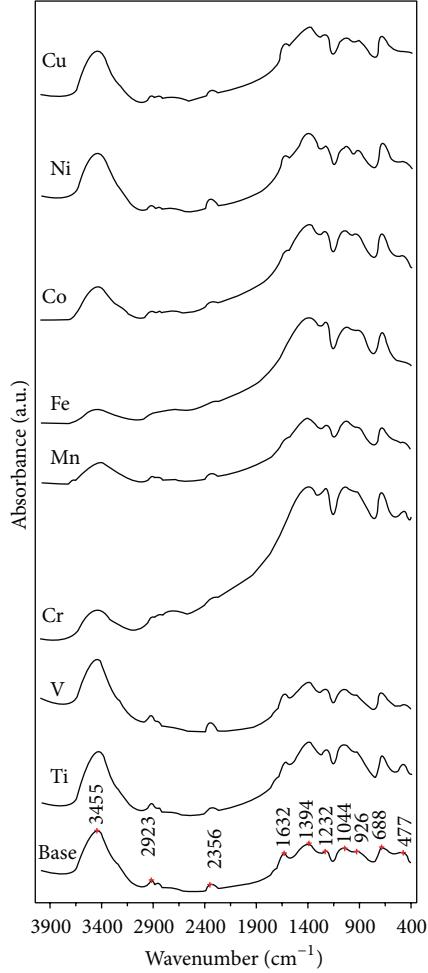


FIGURE 3: FT infrared absorption spectra of undoped and TMs-doped fluoroborate glasses before irradiation.

The observed strong UV bands in the spectrum of the undoped fluoroborate glass are related to the presence of unavoidable trace iron impurities (mainly Fe^{3+} ions) contaminated within the chemicals used for the preparation of such host glass. ElBatal et al. [11, 12] have identified strong charge transfer UV absorption bands in both lithium borate and sodium borate glasses and have given the same interpretation regarding the fact that the appearance of strong UV bands in the undoped borate glasses is originating from trace ferric ions present as impurities in the raw materials for preparation of the mentioned glasses.

4.2. Interpretation of the Effect of Gamma Irradiation on the Optical Spectra of the Studied Glasses. The observed resolution of an induced visible broad band at about 500 nm can be related to the effect of gamma irradiation on borate glass network itself. Previous irradiation studies on borate glasses have been summarized in the review articles by Bishay [9] and Friebel [10]. These specific articles have agreed that the induced bands generated within UV region are related mostly

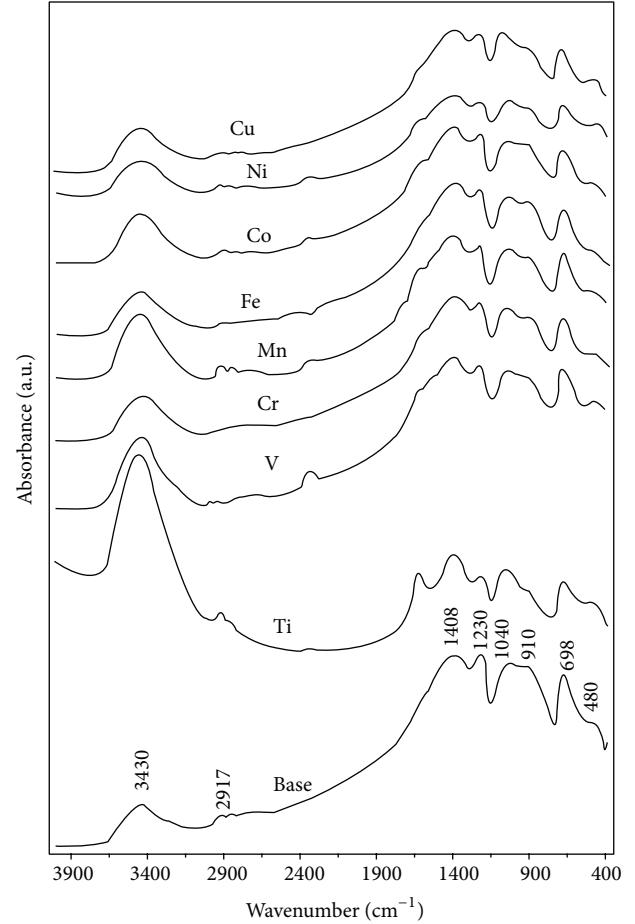


FIGURE 4: FT infrared absorption spectra of undoped and TMs-doped fluoroborate glasses after gamma irradiation (8 MR).

to electron centers and involving sometimes photochemical reactions with trace iron impurities as assumed by Moncke and Ehrt [14] and ElBatal et al. [11, 12]. On the other hand the induced bands generated within the visible region are due to positive hole centers. Therefore, the resolution of an extra induced broad band in the visible region at 500–510 nm with gamma irradiation in all undoped and TMs-doped glasses can be related to positive hole center from the borate glass matrix through the generation of either nonbridging oxygen hole center (NBOHC) or boron oxygen hole center (BOHC) as previously suggested by Bishay [9], Friebel [10], and ElBatal et al. [15, 16].

4.3. Interpretation of the Effect of the Optical Spectra of 3d Transition Metal Ions in Fluoroborate Glasses. In pure oxide glasses transition metal ions form coordination complexes with oxygens as ligands. These oxygens may be of different donor capacity depending on the glass type and composition and thus produce forms of different symmetries of the glass melt which contain ionic species other than oxides, such as halides, and so forth and coordination forms can be identified with anionic substitution [10]. As a consequence of this ligand substitution, the absorption spectra will be expected to

show some changes and the color of the glass can be altered significantly.

It has been recognized that the states of TM ions in binary lithium borate [11] and sodium borate [12] glasses are mainly in the higher oxidation or tetrahedral coordination. The detailed interpretations of the various 3d TM ions are summarized as follows.

4.3.1. Titanium-Doped Glasses. Titanium ions can exist in glass as tetrahedral and trivalent oxidation states [17]. Ti^{3+} ions belong to the $3d^1$ configuration and thus only exhibit a single visible band at 440–540 nm and sometimes show a shoulder at 650–750 nm due to Jahn-Teller distortion [17]. On the other hand, Ti^{4+} ions belong to d^0 configuration and therefore give no visible bands but exhibit ultraviolet absorption. The spectral curve of this TiO_2 -glass reveals the same spectrum observed from the undoped base glass. The spectrum shows no visible bands indicating the absence of trivalent titanium ions. The Ti^{4+} ions are known to exhibit an UV band but no indication is observed except the presence of strong charge transfer UV absorption with two peaks due to trace trivalent iron (Fe^{3+}) present as impurities. It seems that these specific strong UV bands of Fe^{3+} impurities mask or retard the appearance of any UV band related to Ti^{4+} ions.

4.3.2. Vanadium-Doped Glass. The spectrum of this glass reveals an extra strong UV band at 349 nm beside the two strong charge transfer bands due to trace iron (Fe^{3+} ions) present as impurity. Vanadium can exist in glass in three valences: V^{3+} , V^{4+} , and V^{5+} [17]. The trivalent (V^{3+}) ions exist in distorted octahedral coordination with oxygens and show characteristic bands around 400 and 600 nm. Tetravalent vanadium ions exist as vanadyl (VO^{2+}) ions which exhibit weak peaks at about 420, 780, and 1000 nm, while pentavalent vanadium (V^{5+}) ions belong to d^0 configuration and only show an UV band. The extra UV band indicates that this glass favors the pentavalent vanadium state in measurable percent.

4.3.3. Chromium-Doped Glass. This glass reveals an extended UV-visible spectrum showing additional two strong UV bands and two visible bands. Chromium ions are known to be able to exist in glass in two different oxidation states, the trivalent and the hexavalent [18, 19]. The two strong UV bands at 349 and 378 nm are related to Cr^{6+} ions either present as $(CrO_4)^{2-}$ groups or Cr^{6+} ions [17]. The two visible bands at 431 and 615 nm are correlated with trivalent chromium present in octahedral coordination [17]. It is evident that this host glass favors the high hexavalent state to be present as higher intense bands but the lower trivalent chromium ions are present as secondary percent.

4.3.4. Manganese-Doped Glass. This glass exhibits additionally a small broad band centered at 444 nm surplus to the strong charge transfer UV bands previously related to trace iron ferric ions present as impurities within the chemicals.

This new broad band is attributed to the presence of trivalent manganese ions in octahedral coordination [17].

No indication is found for divalent manganese ions which possess spin-forbidden low-intense band at 410 nm. The host fluoroborate glass favours the high valence manganese (Mn^{3+} ions) but with low intense broad band.

4.3.5. Iron-Doped Glass. This Fe_2O_3 -doped glass exhibits an additional small broad centered at 414 nm. This new band at 414 nm is resolved due to the addition of 0.2% Fe_2O_3 as dopant to the composition of the host glass and indicates its relationship to ferric iron (Fe^{3+}) added. The same postulation was introduced and adopted by several authors [18–20].

4.3.6. Cobalt-Doped Glass. This CoO -doped glass reveals an additional broad absorption with two distinct peaks at 491 and 556 nm and followed by a small peak at 725 nm. These additional peaks are related to the presence of cobalt ions in the divalent state in two coordinations; the octahedral is identified at 491 nm and the tetrahedral coordination at 556 and 725 nm. The presence of two coordination states at the same time can be related to the similarity of the ligand stabilization energies of the two coordination states as revealed by several authors [18, 19].

4.3.7. Nickel-Doped Glass. The NiO -doped glass exhibits the same spectrum as that for undoped base glass besides the appearance of a small band at about 430 nm. This extra band at 430 nm is related to the existence of divalent nickel ions in octahedral coordination which is responsible for this band [18, 19].

4.3.8. Copper-Doped Glass. This CuO -doped glass reveals a spectrum consisting of the two charge transfer UV bands due to trace ferric ions and an additional very broad band centered at 794 nm due to divalent copper ions (Cu^{2+}) in octahedral coordination [18, 19].

4.4. The Interpretation of the Effect of Gamma Irradiation on the Optical Spectra of 3d TMs Doped Fluoroborate Glass. The experimental data indicate that the optical spectral results of all the TMs-doped glasses after irradiation reveal the same induced visible band observed with the undoped glass except the two Cr-doped and Cu-doped glasses. Such induced visible band can be related to being generated by gamma irradiation through the formation of positive holes from the borate glass matrix by forming nonbridging oxygen hole center (NBOHC) or boron oxygen hole center (BOHC) as assumed by Bishay [9] and Friebel [10].

The failure to generate such induced visible hole center in glasses containing chromium and copper ions can be related to some shielding effect of these two TM ions as they compete to capture the liberated positive holes. The same results are previously observed by several authors for chromium ions [17] and for copper ions [18, 19].

4.5. Interpretation of the FTIR Spectra. Figure 3 illustrates the FTIR spectra of the studied glasses consisting of undoped $NaF-CaF_2-B_2O_3$ glass together with samples containing 0.2%

of one of 3d TM ions. It is evident that the constituent vibrational bands are those frequently observed from alkali or alkaline earth oxides borate glasses. Based on such similarity the results can be understood and interpreted on the following basis.

- (a) The similarity of the positions of the vibrational bands due to various BO_3 and BO_4 groups in the present studied fluoroborate glasses and that obtained from alkali or alkaline earth oxides borate glasses can be related to the effect of boron element itself which is considered to be the lightest glass forming element and possesses the smallest mass compared to other network forming elements. Thus the main vibrational modes associated with the borate glass network appear well above 500 cm^{-1} in the mid-infrared [4, 20]. The previously mentioned vibrations due BO_3 and BO_4 groups are well separated from the metal ion site vibrational modes which are active in the far infrared region, that is, below 600 cm^{-1} [4, 20].
- (b) The support of the assumption that boron is the main active and responsible for the observed results comes from the formation of similar BO_3 and BO_4 groups whatever the percent of replacement of oxygen anions by fluorine anion.
- (c) The absorption observed in the region $800\text{--}1200 \text{ cm}^{-1}$ is related B–O band stretching vibrations of BO_4 tetrahedra. There is no modifier oxide, so it is suggested by various authors [5–7] that B_2O_3 is partly modified only with NaF and CaF_2 . Various authors [6, 8] suggested that the formed structural units $[\text{BO}_{3/2}\text{F}]^-$ distorted tetrahedra are the most probably formed oxyfluoroborate units.
- (d) The absorption peaks in the region $1200\text{--}1600 \text{ cm}^{-1}$ are attributed to stretches of B–O in BO_3 or (BO_2O^-) units [4, 21].
- (e) The absorption bands in the region $400\text{--}550 \text{ cm}^{-1}$ can be related to vibrations of metal ions in their modifying sites (e.g., Na^+ and Ca^{2+}) as suggested by several authors [20, 21].
- (f) The observed maintenance of the characteristic vibrational bands due to various borate groups upon the introduction of any of the 3d TM ions can be related to the presence of transition metal ions in modifying positions not affecting the structural borate units together with their presence in low doping content (0.2%).

4.6. Interpretation of the Effect of Gamma Irradiation on the FTIR Spectra. The observed maintenance of the main characteristic vibrational bands due to triangular and tetrahedral borate groups upon gamma irradiation can be related to the stability of these constitutional building units being unaffected by irradiation. The minor change in the intensities of some vibrational bands can be related to some limited changes in the bond angles or bond lengths of the mentioned units. Some authors [22–24] have suggested such assumption

and introduced some routes for these changes upon irradiation. Earlier, Primak [22] assumed that the compaction in vitreous silica that originated upon irradiation can be related to the measured changes in the bond angle of Si–O–Si bonding. Later, Hobbs et al. [23] described some sort of changes in the structure of glass produced by irradiation. They assumed that the generation of Frenkel pair effectively breaks some of the connectivity of the network and some SiO_2 units may relax into a triangular or broken linkages by irradiation which evidently results in level structure collapse and rebinding. Piao et al. [24] described the mechanism of radiation-induced compaction by assuming that, during irradiation, ionization produces electron-hole pairs, providing paths for bond change and rearrangement and thus reducing the constraints on structural relaxation. The relaxation process releases some of the excess energy stored in the structure, accompanied by a decrease in the arrangement of bridging bond angle. Another postulation is advanced which assumes that irradiation can cause minor variations of the percent of (BO_3) and (BO_3F) and this necessitates further studies for different glass compositions and with varying doses of gamma irradiation. It can be added that ElBatal et al. [11, 12, 15, 16, 25] have identified that the main structural building groups within borate and silicate glasses remain unchanged by gamma irradiation and the effects are pronounced on IR bands at about 1640 cm^{-1} and 3450 cm^{-1} which are related to water and OH vibrations because they are loosely situated in the glass network as loose ends or as modifiers.

In brief, the minor changes in the intensity of some IR bands can thus be related to suggested changes in the bond angles and/or bond lengths of the shielding units as suggested by several authors [10, 11, 16].

5. Conclusion

Optical absorption spectrum of undoped $\text{NaF-CaF}_2\text{-B}_2\text{O}_3$ glass reveals strong UV absorption bands which are attributed to trace iron (Fe^{3+}) impurities. TMs-doped (0.2%) samples show characteristic absorption bands related to respective TM ions and they exhibit high valence states except in few cases (e.g., Ni and Co are only divalent ions). Gamma irradiation produces within the optical spectra of undoped and all TMs ions-doped glasses except (Cr, Cu) an induced visible band at $500\text{--}510 \text{ nm}$ which is related to boron oxygen hole center or nonbridging oxygen hole center. The absence of this induced positive hole center in Cr-doped and Cu-doped samples is related to some shielding effect of these two TM ions. Infrared absorption spectra of the studied glasses show repetitive characteristic IR vibrational modes due to BO_3 and BO_4 in their separate wavenumber positions. NaF and CaF are assumed to modify the BO_3 groups through forming mostly BO_3F tetrahedra which resemble BO_4 formed by the sharing of alkali or alkaline earth oxides. TMs ions did not show variations in the FTIR spectra being present in low doping level (0.2%) and situated as modifiers in interstitial positions within the glass network.

The effects of gamma irradiation on the FTIR spectra are limited to the variations in the intensities of the same bands

which are related to changes in the bond angles and bond lengths as measured by some authors or in the percent of (BO_3) and (BO_3F) units.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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