



Effect of gamma radiation on ultraviolet, visible and infrared studies of NiO, Cr₂O₃ and Fe₂O₃-doped alkali borate glasses



F.A. Moustafa^a, A.M. Fayad^{a,*}, F.M. Ezz-Eldin^b, I. El-Kashif^c

^a Glass Research Department, National Research Center, Cairo, Egypt

^b National Center for Radiation Research & Technology, Nasr City, Cairo, Egypt

^c Physics Department, Faculty of Education, Suez Canal University, Arish, Egypt

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ABSTRACT

Borate glasses with basic composition $xR_2O \cdot (100 - x)B_2O_3$ where $R = Na, K$, were colored by doping with one of transition metal ions Ni, Cr, Fe or doping with mixing of them. The effect of glass composition and gamma ray irradiation on the optical and infrared absorption spectra was studied and interpreted in terms of structural concepts. A resolution of the observed absorption spectra showed the existence of each transition metal ion in the possible coordination state according to the composition of the glass. The IR measurements reveal characteristic absorption bands due to various groups of triangular and tetrahedral borate network. The introduction of trace amounts of mixed dopants Cr₂O₃, Fe₂O₃ and NiO has no major effect on the structure of the studied glasses. The induced absorption spectra exhibit the characteristic absorption bands caused by the intrinsic base borate glass and the respective transition metal ions. The response of the doped glasses to gamma ray irradiation is assumed to be related to the formation and annihilation of the induced color centers.

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1. Introduction

Borate glasses are very interesting amorphous materials considering their specific structure and physical properties [1] and are also interesting as inorganic hosts for transition metal ions. In the recent past, the technological applications have created enormous interest on the studies of oxide glasses. The most important part of the study on the alkali borate glasses containing transition metal ions shows non-linear behavior, which has applications in solid state devices, electro-optic modulators, electro-optic switches, electric and electro-optical devices and non-linear optical parametric converters [2].

The formation and the nature of the color centers in different types of glasses have received a considerable attention [3]. The presence of elements with multiple valences may either enhance the coloration by the valence change or reduce the color center formation by trapping the released electrons [4].

Transition metal ions are known to influence the optical, electrical and magnetic properties of glasses due to their high sensitive response to the changes in the surrounding cations and their ability to possess more than one valence state. Further, these ions can be used as better candidates to probe the glass structure due to their broad radial distribution of outer d-orbital electron functions and their sensitive response to the surrounding cations [5].

Weyl [6] concluded that the color change in glasses containing nickel is not caused by a change in the valence of nickel since nickel is always in

divalent state with different numbers of surrounding oxygens. Various authors [7–10] have related and discussed the detailed absorption spectra of Ni ion in alkali borate glasses from the point of view of ligand field theory and stabilization energies of both octa- and tetrahedral coordinations are very close indicating the possible occurrence of these two states together.

Chromium ions dissolved in glasses make them colored and have strong influence over the insulating character and optical transmission of these glasses, since Cr₂O₃ also participates in the glass network forming two valences with different structural units. Chromium may exist in both Cr³⁺ and Cr⁶⁺ states in the glass network. Cr³⁺ ion enters in the network acting as modifier with [CrO₆] structural units whereas Cr⁶⁺ ion enters as network former with CrO₄²⁻ structural units [11].

Iron may occur in a number of oxidation states; however it is usually present in glasses melted under atmospheric conditions in two valence states, namely Fe²⁺ and Fe³⁺ ions. The redox and environment of iron and chemistry of the glass matrix in which it is present are closely inter-related and can substantially influence the resulting optical properties, specifically the UV-visible and IR transmission [12]. The spectra of Fe³⁺ ions in various glasses have been extensively studied [13,14]. It is reported that the trivalent iron ions can take two different coordination sites, i.e., either tetrahedral or octahedral sites in glasses.

By varying the chemical composition of a glass, the local environment of the transition metal (TM) ion incorporated into the vitreous network can be changed, leading to local ligand field homogeneities. So the main objective of this work is using the present spectroscopic studies on Cr³⁺, Ni²⁺ and Fe³⁺ doped borate glasses to ascertain their site symmetries in the host lattice, along with their spectral

* Corresponding author. Tel.: +20 1001574646.

E-mail address: amirafayad@gmail.com (A.M. Fayad).

properties. Also, IR spectral measurements are expected to justify the structural building groups in the host borate glass.

A further aim is to investigate the response of the Cr^{3+} , Ni^{2+} and Fe^{3+} doped borate glasses after gamma irradiation.

2. Experimental details

2.1. Preparation of the glasses

The preparation of the studied glasses was carried out from chemically pure raw materials. B_2O_3 was introduced in the form of orthoboric acid (H_3BO_3). Soda was added in the form of anhydrous carbonate while NiO , Cr_2O_3 and Fe_2O_3 were introduced as such (Table 1).

The well mixed weighed batches were melted in platinum 2% Rh crucibles at a temperature of 1100 °C for 2 h to reach homogeneity. The melts were rotated several times and were cast into preheated stainless steel molds of the required dimensions. The prepared samples were immediately transferred to an annealing muffle furnace regulated at 400 °C. The muffle containing the prepared samples was left to cool to room temperature.

2.2. X-ray diffraction analysis

The amorphous state of some glasses was checked by X-ray diffraction spectra recorded in Shimadzu (Japan) diffractometer type XD-D₁ with copper target and applied voltage of 40 kV and 30 mA anode current.

2.3. Optical absorption spectral measurements

The ultraviolet and visible optical absorption spectra were measured for perfectly polished glass samples of equal thickness (2 mm ± 0.01 mm) before and after gamma irradiation using a recording double beam spectrophotometer (JASCO Corp., v-570, re1.00, Japan) covering the range from 200 to 1000 nm.

2.4. Infrared absorption measurements

The infrared absorption spectra of the TM-doped glasses were measured before and after gamma irradiation at room temperature in the wave number range of 4000–400 cm^{-1} by a Fourier Transform computerized infrared spectrometer type (JASCO Corp., FT/IR-430, Japan).

2.5. Gamma irradiation

A ^{60}Co gamma cell (2000 Ci) was used as a gamma ray source. The glass samples were placed in the gamma cell in the manner that each sample was subjected to the same gamma dose (1 Mrad).

Table 1
The composition of the glass samples studied.

Glass no.	Glass composition (wt.%)					
	B_2O_3	Na_2O	K_2O	NiO	Cr_2O_3	Fe_2O_3
1	95	5	–	0.2	–	–
2	80	20	–	0.2	–	–
3	65	35	–	0.2	–	–
4	95	5	–	–	0.05	–
5	80	20	–	–	0.05	–
6	65	35	–	–	0.05	–
7	95	5	–	–	–	0.5
8	80	20	–	–	–	0.5
9	65	35	–	–	–	0.5
10	95	5	–	0.2	0.05	0.5
11	80	20	–	0.2	0.05	0.5
12	65	35	–	0.2	0.05	0.5
13	95	–	5	0.2	0.05	0.5
14	80	–	20	0.2	0.05	0.5
15	65	–	35	0.2	0.05	0.5

3. Results

3.1. X-ray diffraction analysis

X-ray diffraction investigation of the studied glasses reveals no diffraction peaks in lines or any crystalline phases, and the results as shown in Fig. 1 indicate that the samples prepared were of high quality glasses.

3.2. UV–visible absorption spectra

The optical absorption spectra of the unirradiated glass samples containing 0.2 g NiO are shown in Fig. 2a, and the visible spectrum consists of three absorption bands centered at 425, 670 nm and followed by a broad medium band centered at about 780 nm in the glass composition 95 B_2O_3 , 5 Na_2O , 0.2 g NiO. The two absorption bands at 425 and 780 nm are shifted to 445 and 810 nm, respectively. The band at 670 nm disappeared in the glass composition 80 B_2O_3 , 20 Na_2O , 0.2 g NiO. Two new absorption bands at 545 and 625 nm are observed in the glass composition 65 B_2O_3 , 35 Na_2O , 0.2 g NiO.

The glass samples exhibit different colors which are changed from pale yellowish green to brown with increasing of the soda oxide content.

The optical absorption spectra of the unirradiated glass samples containing 0.05 g Cr_2O_3 are shown in Fig. 2b. The spectrum consists of five absorption bands changed in the range at 370–380, 460, 610–620, 660–665 and 680–700 nm according to the change in the glass composition.

The colors of glass samples changed from rich green to pale yellow-green with increase of the alkali oxide content.

The optical absorption spectra of the unirradiated glass samples containing 0.5 g Fe_2O_3 are shown in Fig. 2c. Four absorption bands are observed at 220, 250, 345 and 460 nm and are shifted to 215, 253, 355 and 475 nm with the increase in the soda oxide content.

The color of glass samples is observed to change from yellow to deep yellow with increase of the soda oxide content.

The optical absorption spectra of the unirradiated borate glass samples containing mixing of the three transition metal oxides: 0.2 g NiO, 0.05 g Cr_2O_3 and 0.5 g Fe_2O_3 are shown in Fig. 2d. The absorption spectra of these borate glasses are generally of a very complex nature because of the presence of Cr_2O_3 , Fe_2O_3 and NiO together. The spectra consist of nine absorption bands extending in the ultraviolet and visible regions centered at 210, 230, 330, 445, 470, 655, 690, 740 and 770 nm.

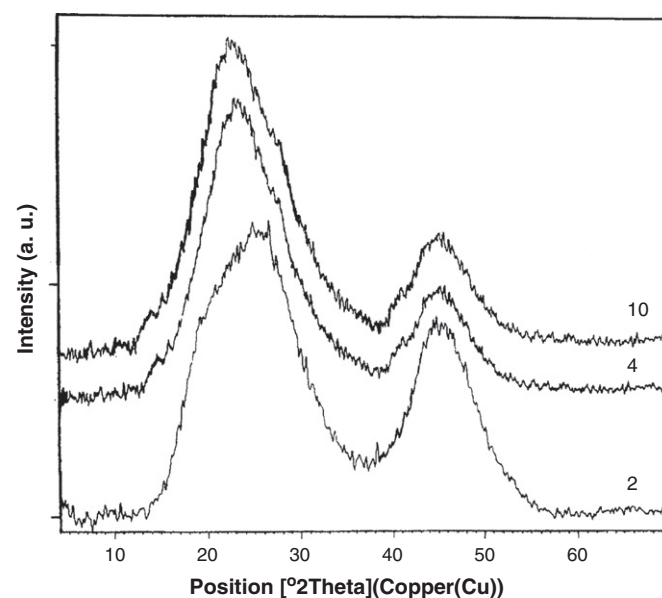


Fig. 1. X-ray diffraction analysis of glass samples. No. 2. Ni-doped soda borate glass, 4. Cr-doped soda borate glass. 10. Combined TM-doped soda borate glass.

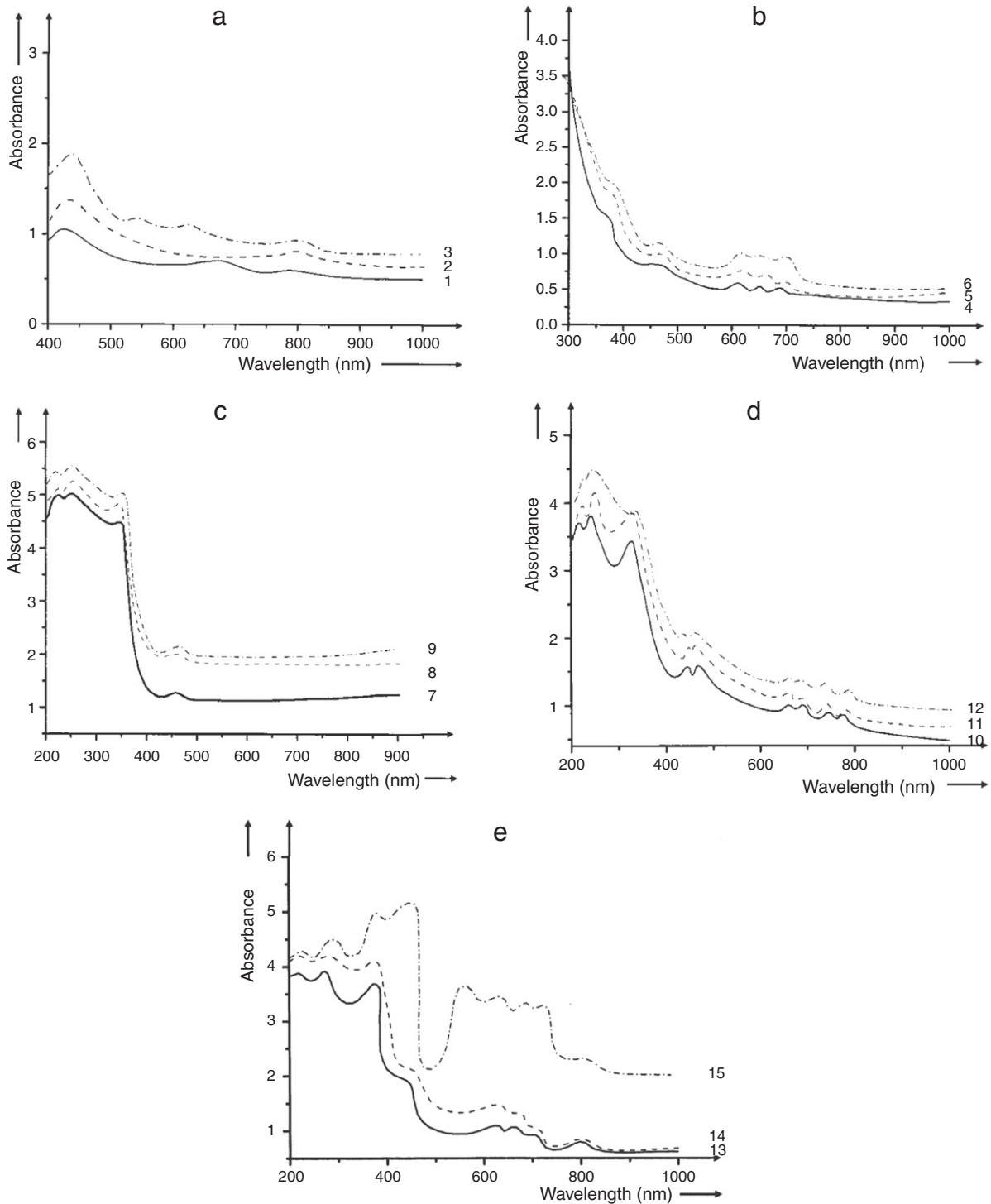


Fig. 2. UV-visible absorption spectra of a. Ni-doped soda borate glass, b. Cr-doped soda borate glass, c. Fe-doped soda borate glass, d. combined TM-doped soda borate glass, and e. combined TM-doped potash borate glass, before gamma irradiation.

The positions of these absorption bands are observed to change according to the change of the base glass composition.

The glasses show a change in color from green to brown with increase of the soda content.

The optical absorption spectra of the unirradiated glass samples in which potash replacing soda containing mixing of the three transition metal oxides: 0.2 g NiO, 0.05 g Cr₂O₃ and 0.5 g Fe₂O₃ are shown in Fig. 2e. The optical spectra consist of eight absorption bands extending in the ultraviolet and visible regions observed at 220, 290, 380, 445,

625, 660, 720 and 800 nm. New absorption band at 545 nm is appeared in the composition containing 35% K₂O.

Inspection of Fig. 3a–e reveals the absorption spectra of glasses after irradiation. The following changes are observed:

- 1 The ultraviolet and visible absorption bands show an increase in their intensities with marked shift to longer wavelengths with radiation.
- 2 Appearance of new absorption band at 625–650 nm in sodium borate glasses containing 0.5 g Fe₂O₃.

3.3. Induced spectra

Fig. 4a–d illustrates the induced spectra of borate glasses which represent the change in optical density of the irradiated glass subtracted from the optical density of the unirradiated base glass versus wavelength.

3.4. Infrared absorption spectra measurements

The infrared absorption spectra of the samples studied are represented in Fig. 5a from which it is obvious that the infrared absorption spectra exhibit three groups of bands: (a) the main vibrational modes of borate network appear well above 500 cm^{-1} in the mid-infrared

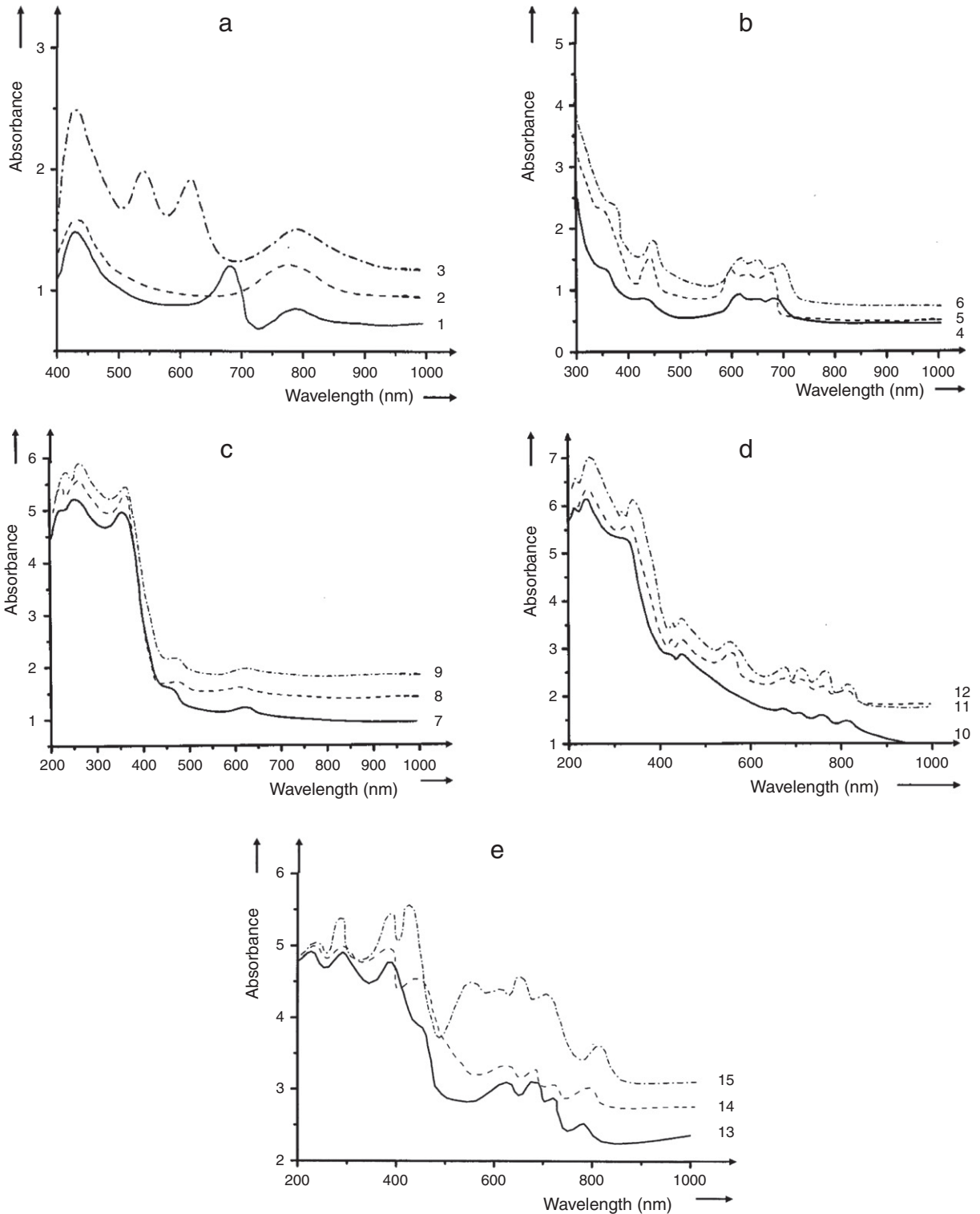


Fig. 3. UV-visible absorption spectra of a. Ni-doped soda borate glass, b. Cr-doped soda borate glass, c. Fe-doped soda borate glass, d. combined TM-doped soda borate glass, and e. combined TM-doped potash borate glass, after gamma irradiation.

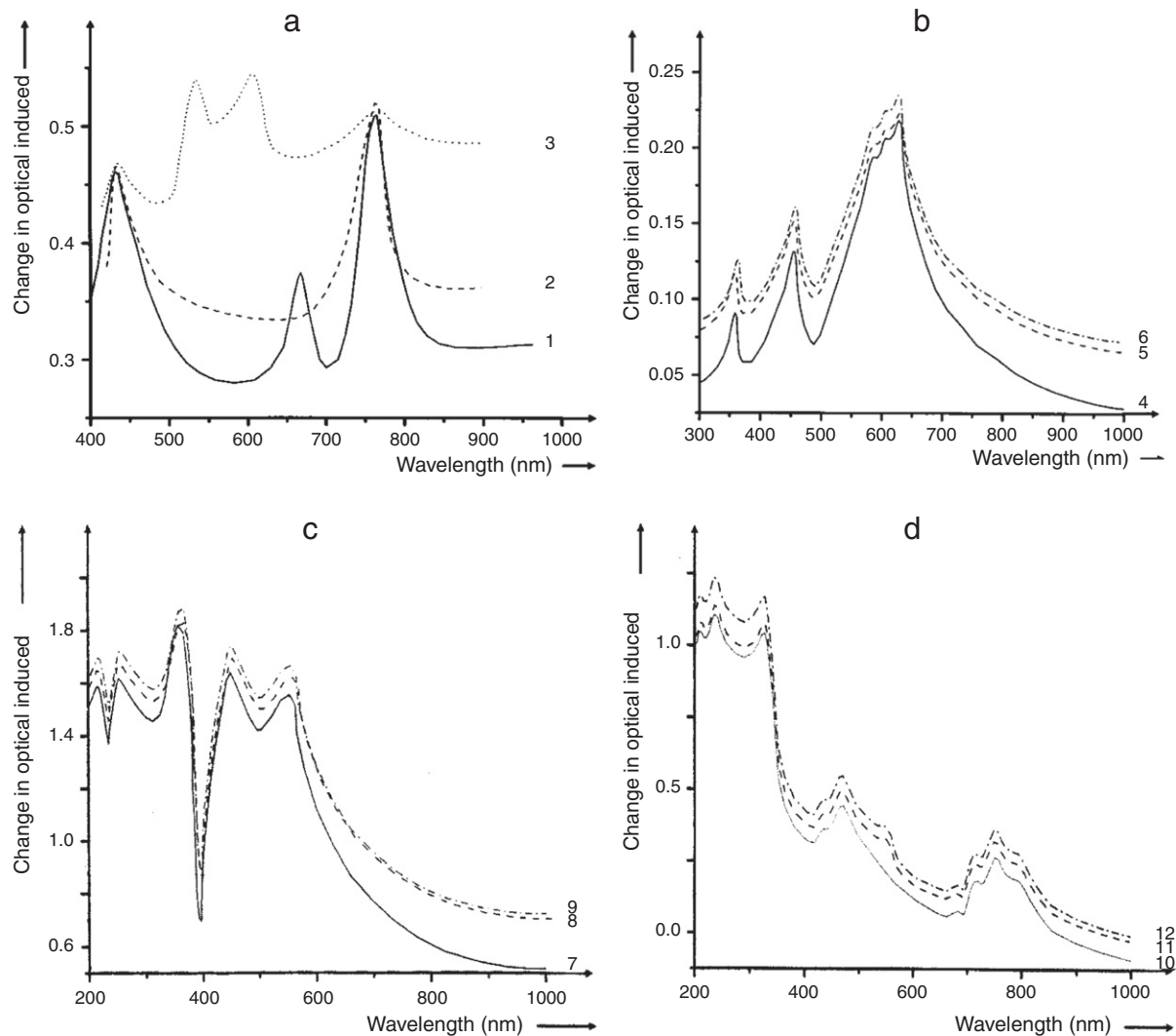


Fig. 4. Induced spectra of a. Ni-doped soda borate glass, b. Cr-doped soda borate glass, c. Fe-doped soda borate glass, and d. combined TM-doped soda borate glass.

[15]. (b) Also, the spectrum reveals some of the vibrational sites active in the far-infrared, i.e., 600–400 (beginning of measurements), (c) and the near-infrared vibrational modes which include the OH and water related vibrations.

In the mid-region, Fig. 5a shows five prominent absorption bands at about 699, 825, 1020, 1464, 1643 cm^{-1} together with connected less intense bands or kinks in the ascending or descending lobes of these sharp bands at about 935, 1137, 1270, and 1347 cm^{-1} . Also, the spectrum was revealed in the far-infrared small peak at about 530 cm^{-1} . A small band at 2245 and 2620 cm^{-1} followed by a medium broad band at 3050 cm^{-1} and a very broad intense band with two distinct peaks at 3375 and 3534 cm^{-1} are also obvious in the near-infrared region.

It is obvious that the absorption spectra of borate glass containing chromium oxide reveal some broadening in some absorption bands with small peaks at the same position as distinct absorption bands in the other spectra.

The introduction of TM ions has only minor effects on the IR spectra of the studied alkali borate glasses because it is added in low percent indicating that the structural groups remain unchanged giving their characteristic vibrations.

The IR spectra (Fig. 5b) reveal two marked changes in comparison with the same IR of these samples before irradiation. The first observation is that the intensities of almost all IR bands after irradiation are relatively lower than that shown in the IR spectra before irradiation.

The second observation is the rounded peaks of almost all absorption bands. The main spectral bands due to borate structural groups are shown to be persistent.

4. Discussion

4.1. Interpretation of the absorption spectra of NiO-doped glasses

The spectra of sodium borate glasses with Ni addition exhibit (Fig. 2a) different absorption bands according to the change in the glass composition. The absorption bands at 425 and 770 nm are assigned to the two spin allowed transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ while the other one at 670 nm is attributed to spin forbidden transition ${}^3A_{2g}(F) \rightarrow {}^1E_{3g}(D)$ due to d–p orbital mixing which takes place due to the fact that the ion is not at the center of symmetry [16]. The absorption band at 670 nm is disappeared by increasing the soda oxide content due to the formation of tetra borate groups and the increase of the nonbridging oxygen and hence a decrease in ligand field strength [17,18]. In borate glass of soda content at 35%, the non-bridging oxygen ratio increases and the polarization effect of oxygen ions is expected to be suitable for the formation of tetrahedral coordinated ions. The double absorption bands at 545 and 625 nm, of transitions ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$, are due to the nickel ion in the tetrahedral coordination [10]. Both the changing of color samples and optical spectra of examined soda-borate glasses indicate that Ni occurs in these glasses as divalent Ni^{2+} in both

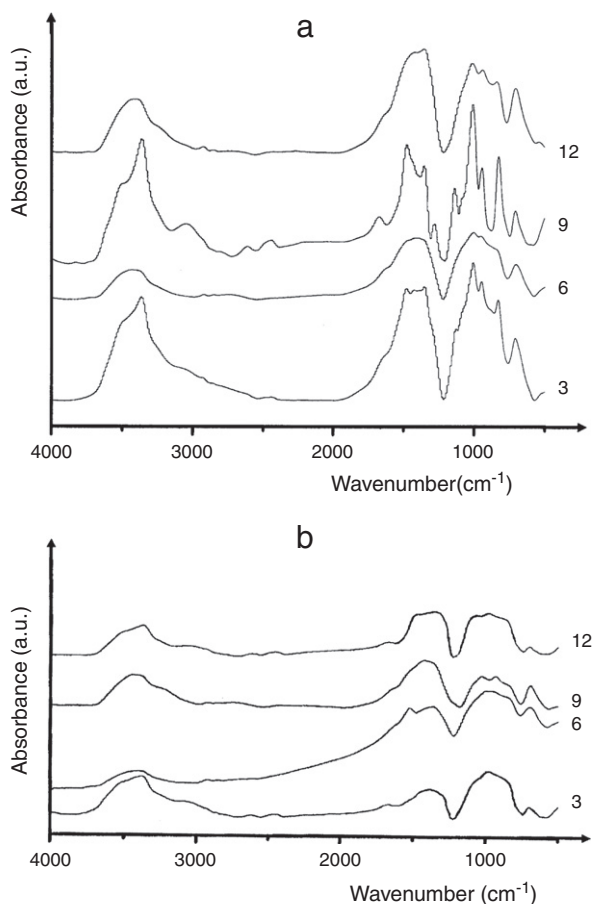


Fig. 5. Infrared absorption spectra of the studied TM-doped soda borate glass, a. before gamma irradiation, and b. after gamma irradiation.

octa- and tetrahedral coordination with oxygen ions which are in equilibrium.

4.2. Interpretation of the absorption spectra of Cr_2O_3 -doped glasses

Cr^{3+} (d^3) ions tend to occupy approximately octahedral sites in crystals and also in glasses [19]. From the ligand field stabilization energies and the fact that the Cr^{3+} ions have only been reported in regular and slightly distorted octahedral complex, the spectra have been analyzed (Fig. 2b). The bands observed at 370, 460 and 650 nm are assigned to spin allowed transitions ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$, ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{F})$ and ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, respectively. In addition, the absorption spectrum shows fine structure in the vicinity of the ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ band (Fig. 2). The dips at about 670 and 635 nm are due to the transitions ${}^4A_{2g}(\text{F}) \rightarrow {}^2E_{2g}(\text{F})$ and ${}^4A_{2g}(\text{F}) \rightarrow {}^2T_{1g}(\text{F})$. The 2E and 2T states acquire their spin-allowed characters via spin orbit interaction with the broad iso-energetic ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ transition, and this interaction results in the presence of a Fano-antiresonance leading to the observed dips [20]. These observations indicate that the presence of chromium ion in both Cr^{3+} state in octahedral environment in the glass matrix and the hexavalent chromium (Cr^{6+}) ions is represented by the extra UV band at about 370 nm [16] and the yellow-green color shade of soda-borate glasses.

4.3. Interpretation of the absorption spectra of Fe_2O_3 -doped Glasses

Fe^{3+} ions have the $3d^5$ configuration which is of special interest in that it is the only configuration for which there are no spin-allowed

transitions possible and only weak bands may occur corresponding to spin-forbidden transitions. The d^5 configuration is of particular interest as the energy diagram for it applies to complexes of both octa- and tetrahedral symmetry [21].

While in Fe^{2+} (d^6), present usually in octahedral coordination, the energy level diagram in octahedral symmetry consists essentially of a single absorption band corresponding to spin allowed transition together with several weak lines and absorption bands corresponding to spin forbidden transitions [22,23].

The absorption spectra of the sodium borate glasses doped with iron oxide (Fig. 2c) exhibit four absorption bands at 220, 250, 345, 460 nm: The two ultraviolet absorption bands at 220 and 250 nm may be considered as charge transfer bands for ferric ions. Also, they are attributed to be due to raw material impurities [24]. From the Tanabe–Sugano energy level diagram given for d^5 configuration, the bands observed at 460 and 345 nm have been assigned to the ${}^6A_{1g}(\text{S})\text{--}{}^4T_{2g}(\text{G})$ and ${}^6A_{1g}(\text{S})\text{--}{}^4T_{2g}(\text{D})$ transitions, respectively. The observed band positions are characteristic of Fe^{3+} ions in the distorted octahedral environment [25–27]. The change in the position and intensity of the absorption bands that may arise from the increase in the soda oxide content caused a decrease in ligand field strength and an increase in d–p orbital mixing [8]. The optical spectra and the color changing of the soda-borate glass samples indicate that Fe occurs in these glasses predominantly as trivalent Fe^{3+} in octahedral coordination.

4.4. Interpretation of the absorption spectra of mixing TMs-doped soda or potash borate glasses

The combined glass containing 0.2 g NiO , 0.05 g Cr_2O_3 and 0.5 g Fe_2O_3 produced a change in color from green to brown according to the change in soda or potash content. It is observed that the green-colored chromium ions mask the colors of nickel and iron ions in low soda or potash content but the brownish nickel ions in tetrahedral coordination mask the colors of chromium and iron ions in high soda or potash content. However, the characteristic optical absorption bands (Fig. 2d & e) of nickel ions of both octahedral and tetrahedral coordination states are clearly identified together with the absorption bands of chromium and ferric ions [28]. The result illustrates the variation of the coordination states as in the case of nickel and iron ions or the valence states as in the Cr^{3+} , Cr^{6+} with the increase in the soda or potash content by recognition of the characteristic ultraviolet or visible absorption bands for different states for each ion.

4.5. Interpretation of the effect of gamma irradiation

The nature of radiation damage in glass depends on the type (i.e. ionizing versus particle) and energy of radiation impinging on the material. The resultant effects may be divided into three categories [29]:

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

The radiation damage processes that take place in glasses are generally the same as that occur in crystals. It is accepted that multivalent impurities, such as transition metal, can easily trap electrons or positive holes when irradiated. The transition metal ions can compete with the intrinsic defects already present in the glass to trap the electrons and holes produced by irradiation. The capturing process depends strongly on the nature of the transition metal ion and its concentration, as well as on the type and state of the host glass. Recent studies have been carried out on collective 3d transition metal ions including (Ni, Cr and Fe) and investigating the effect of the gamma irradiation on UV-visible absorption spectra in various host glasses [30]. Such studies have reached to several important parameters concerning the role of 3d transition metal in different host glasses

on the irradiation mechanism and such parameters can be summarized as follows:

1. Gamma irradiation is accepted to produce pairs of electrons and positive holes generated during the irradiation process. 3d transition metal ions are assumed to capture electrons or holes and subsequently are changed to lower or higher valence states, respectively. Such photochemical reactions include the capturing of the released electrons or holes and hence they share in the shielding process which was clearly identified when the 3d transition metal ions were present in high content [31].
2. High alkali borate favors the presence of the 3d transition metals in their higher valence states or tetrahedral coordination as concluded by other author [32].
3. Such shielding or retardation behavior was efficiently observed with glasses containing high atomic weight elements such as PbO or high Bi₂O₃ contents.

The effect of transition metal ions on the formed induced defect color centers can be outlined and interpreted as follows:

1. The Ni-doped glass reveals before and after irradiation the same absorption bands different in their intensities or little in their positions with increase in alkali oxide content. This spectrum seems to originate from the combined sharing of the Ni²⁺ ions in the octahedral and tetrahedral coordination [33,17]. The induced spectrum reveals strong visible bands extending from 440 nm to 770 nm which are mostly related to nickel ions and the base host borate glass.
2. In the Cr-doped glass, the induced bands reveal one low UV band and two visible bands at about 450 nm followed by an induced broad and prominent visible band splitting into three peaks in ascending order at 570, 590 and 640 nm. The overall induced spectrum indicates a retardation of the UV bands by gamma irradiation. It is obvious that the presence of chromium ions suppresses the UV bands and the visible spectrum reveals an induced positive hole band related to the host sodium borate glass. A similar result was reached by El-Batal and Ezz El Din [34] in their studies on Cr-doped in alkali-alkaline earth borate glasses.
3. The induced spectra of Fe-doped glass reveal strong charge transfer of three ultraviolet bands with two visible bands at 445 and 560 nm. It is suggested that gamma irradiation produces induced radiation defects (mainly electron defects) in the ultraviolet region and positive holes in the visible region. Also some defects are generated through the possibility of photochemical reactions leading to the transformation of Fe²⁺ to Fe³⁺ ions. This spectrum represents the spectral features expected for Fe³⁺ ions as expected from its dominance in alkali borate glass [8,17], and the effect of iron species is as dominant as the response of the host glass.
4. The induced spectra of the three transition metal doped sodium borate glass, reveal three small UV absorption bands followed by six and changed to seven visible absorption bands by increasing alkali oxide content. The effect of transition metal ions can be explained by assuming that these ions are available as potential traps for the radiolytic electrons and holes [29]. In most cases, the trapping of charges by the transition metal ions seems to be favored and the response of the glass depends primarily on the type and concentration of these dopants (or impurities). It is important to note that the presence of the dopants does not alter the intrinsic trapping sites of the glass. Rather, by providing alternate sites, they retard the formation rate and increase the recovery rate of the intrinsic color centers. It is speculated that many transition metal ions compete successfully with the intrinsic traps for the radiolytic charges [35].

4.6. Interpretation of infrared absorption spectra

Infrared spectra of crystalline and vitreous borates have been used as a basis for the qualitative identification of glass-forming structural

units in these glasses [36,37]. Due to the structural disorder or non-periodic arrangement, a complete vibrational analysis is done primarily by comparing the spectra of those glasses with those of corresponding crystalline borate for which the structures are known. The realization and interpretation of the IR spectra have been carried out in agreement with the concept adopted by Tarte [38] and Condrate [39] about the independent vibrations of different groups. Also, the recent review on infrared studies of borate glasses [40] is borne in mind, from which the IR absorption bands observed in the studied borate glasses can be assigned as follows:

1. The IR bands at 850–880, 900–1000 and 1030–1080 cm⁻¹ can be attributed to the vibrations of tetrahedral borate groups mainly diborate and possibly triborate and pentaborate groups. The asymmetric stretching vibrations of tetrahedral borate BO₄⁻ units are active in the 800–1200 cm⁻¹ range as evidenced by the appearance of the strong band at about 1020 cm⁻¹ and a small peak at 825 cm⁻¹.
2. The high-frequency absorption (1350–1550 cm⁻¹) cannot easily be attributed to specific borate units, because most of the borate groups absorb in this region. However, the modes of boron–oxygen triangular units (BO₃ and BO₂O⁻) are absorbing at (1200–1650 cm⁻¹) and specifically the bands at 1270, 1347, 1464 and 1643 cm⁻¹.
3. The low frequency region of the mid-infra (550–800 cm⁻¹) is dominated by the bending vibrations or deformation modes of various borate units and the medium band at 699 cm⁻¹ represents this mode.
4. The far-infrared band at about 530 cm⁻¹ is correlated with alkali ions in two residing sites as bridging and non-bridging types as shown by Kamitsos [40].
5. The bands extending from 2400 to 4000 cm⁻¹ including the characteristic near-infrared absorption bands are due to water, OH and B–OH vibrations as have been attributed by Doremus et al. [41] and others [42,43].
6. The IR spectra of nickel, chromium and iron-doped borate glasses are almost similar. Various authors [17,44] have been revealed that the divalent nickel ions are mostly housed in interstitial positions within the borate network without any disturbance on the main structural group arrangement. So it is obvious that the minor concentration of chromium and iron ions has no measurable effect on the structural building groups usually observed in borate glasses [45].

Table 2 depicts the infrared absorption bands and their assignments and references.

4.7. Interpretation of the effect of gamma irradiation on the IR spectra of the studied glasses

The IR spectra (Fig. 5b) after irradiation reveal that the main vibrated groups appeared in the same numbers and positions as shown in the unirradiated curves, which indicates that the overall triangular or tetrahedral structural units of the studied glasses retain in general with their arrangement. The observed small changes can be realized and interpreted on the following basis:

- (1) The appearance of the rounded peaks and the disappearance of the sharpness or obvious splitting can be related to the possible expectation of the tendency to more randomness or amorphicity of the structure due to the effect of irradiation. Hobbs et al. [49] assumed that the radiation causes the generation of the so-called Frenkel-pair defects which effectively break the connectivity of the network. They also added that accumulation of such broken linkages evidently results in local structural collapse and stochastic rebinding.
- (2) Recently, Piao et al. [50,51] describe the mechanism of radiation-induced defect by assuming that during irradiation, ionization process produces electron-hole pairs, providing paths for bond rearrangements, reducing the constraints on structural relaxation.

Table 2
Position and assignment of some infrared absorption bands.

Position of absorption bands (cm ⁻¹)	Assignment
3500	Fundamental free OH stretching vibrations [46]
2800–2400	Very strongly hydrogen bonded OH stretching vibrations [46]
> 1400	B–O symmetric stretching vibrations of various borate groups [40]
1400–1340	Stretching vibrations of metaborate groups [40]
1250	B–O stretching vibrations involving mainly the linkages of oxygen connecting different groups [40]
1200–850	B–O asymmetric stretching vibrations of tetrahedral BO ₄ units [15]
1065–930	B–O stretching vibrations of BO ₄ tetrahedral in pentaborate units [15]
880–800	Stretching vibrations of tri, tetra and pentaborate groups [15]
700	Bond bending vibrations of bridging oxygen atoms [47,48]
550	Motion of alkali ions [15]

The relaxation process releases some of the excess energy stored in the structure, accompanied by a decrease of the average bridging bond angle. Due to the absence of regular structure, the relaxation involves long range effects and essentially the entire structure participates.

- (3) A similar result and adopting the same conclusion were reached by El Batal et al. [52,53] on the effect of gamma irradiation on the IR spectra of ternary silicate glasses containing mixed CoO + NiO or single CoO.

5. Conclusion

The changes in optical absorption of alkali borate glasses containing mixed NiO + Cr₂O₃ + Fe₂O₃ dopants are related to the coordination or valence states of the transition metal ions.

Infrared spectroscopic measurements indicate the presence of absorption bands due to characteristic borate groups (BO₃ and BO₄) as the main glass consisting groups. The effects of the small studied concentration of each TM dopants on the FTIR spectra are limited within the major glass constituents.

Gamma irradiation causes some variations in the optical spectra of the studied glasses due to the generation of induced defects through the released electron or positive holes during the irradiation process of the studied glasses. Also, the effects of gamma irradiation on the IR spectra of all glasses are concentrated on the intensities of some bands and the main vibrational units remain mostly unchanged in their position. These limited changes are related to more amorphicity or disorder by irradiation or on some variations in the bond angles and/or bond lengths of the structural units.

Experimental UV–visible data indicate the suitability of the studied TM-doped glasses in the design of the chemical glass compositions of defined color or in the research concerning the mechanism of color in amorphous materials.

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