Silicon (2018) 10:49–57
DOI 10.1007/s12633-015-9354-z

ORIGINAL PAPER

Effect of CoO and Gamma Irradiation on the Infrared Absorption Spectra of Lithium Borate Glasses

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Received: 1 December 2014 / Accepted: 1 September 2015 / Published online: 10 December 2015

Abstract Undoped and cobalt-doped lithium borate glasses (LBG) of various compositions, by varying cobalt contents were prepared by a conventional melt quenching technique. The density and molar volumes of the glass samples were estimated and; infrared absorption spectra were measured in the spectral range 400–1600 cm^{-1}before and after an irradiation dose of 50 kGy and 200 kGy. Experimental results showed that the density of studied samples increased as CoO increased while the molar volume decreased. FT-IR spectra of the prepared samples have been analyzed by the deconvolution of the spectra. A deconvolution technique is presented to make use of the BO_4 data and follow the change in the modifier and former fractions of CoO. FTIR was also used to study the glass system before and after gamma irradiation. The experimental results clearly indicate that after irradiation a significant change in the structure of the LBG glass network is observed. The modifying action of CoO on the glass composition is also studied. The glasses doped with 5 wt% of CoO are relatively more radiation resistant than the other compositions.

Keywords Lithium borate glass · CoO · Gamma irradiation · IR · deconvolution

1 Introduction

B_2O_3 is one of the best-known glass formers and is present in a variety of commercial glasses. It is often used as a dielectric and insulating material and it is known that borate glass is a good shield against gamma radiation. It is also of academic interest because of the occurrence of the boron anomaly [1, 2]. The boron atom in borate crystals and glasses is usually coordinated with either three or four oxygen atoms forming BO_3 or BO_4 structural units.

In the alkali borate glass systems, each alkali oxide is associated with a proportional quantity of B_2O_3, so that the number of the structural units depends on both the nature and the total concentration of the added modifiers, and can often give rise to tightly organized structures resulting in intermediate order [3–7]. Transition metal (TM) ions can exist in different valence or coordination states when integrated in the glass structure. The cobalt ions are commonly found in glass as divalent Co^{2+} [8],whereas iron, tungsten, molybdenum, and others, can be present in more than one valence state, depending on the type and properties of the modifiers and formers within the glass, size of the ions in the glass structure, their field strength, etc. Depending on the valence state, the ions of TM can occupy substitution or interstitial positions in the glass network [9].

The deconvolution method is used for analyzing the infrared spectra of borate glasses to determine the concentration of borate structural units. Recently [10, 11] researchers determined the relative concentration of the different borate structural units BO_4 and BO_3. Deconvolution of IR spectra can be considered as a useful tool to extract information about borate glass structure rather than the traditional analyses of IR. X rays and gamma rays can result in the introduction of defects such as discoloration or

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Table 1 Chemical composition of investigated glass (wt%) and corresponding density, molar volume

Sample	Composition in wt%	Density(d)[g/cm^3]	Molar volume(Vm)[cm^3/mol]
G0	$85B_2O_3$ -$15Li_2O$ -0CoO	2.23	40.87
G1	$85B_2O_3$ -$15Li_2O$ -0.1CoO	2.25	40.50
G2	$85B_2O_3$ -$15Li_2O$ -0.2CoO	2.61	35.249
G3	$85B_2O_3$ -$15Li_2O$ -2CoO	2.65	34.717
G4	$85B_2O_3$ -$15Li_2O$ -5CoO	2.67	34.940
G5	$85B_2O_3$ -$15Li_2O$ -10CoO	2.98	32.026

fluorescence, rupture of chemical bonds etc. on interaction with the glass [12].

Interaction of gamma rays with lithium borate glasses doped with cobalt produced secondary electrons from the stable state sites have an excess energy. Such excited electrons may traverse in the glass network depending upon their energy and composition of the glass and are finally trapped, thus forming color centers. The trapping sites may be due to the metal cations which constitute the glass structure, ions of admixtures to the main composition, structural defects or impurities in the glass. Thus, this radiation damage process in borate glasses leads to the formation of (1) boron electron centers, (2) non-bridging oxygen hole centers and (3) boron oxygen hole centers [13]. Consequently, non bridging oxygen (NBO) formation has been studied by infrared spectroscopy using the deconvolution method.

The aim of the present work is to perform a calibration of the data obtained from IR techniques so that BO_4values can be deduced from IR data by quantifying specific peaks contained within the spectra of undoped lithium borate glass and CoO doped glasses by taking into consideration the dual structural role of CoO. It also aims to explore the efficiency of this glass to resist gamma radiation as a function of CoO concentration by investigation of their IR spectra before and after irradiation with different doses of gamma rays.

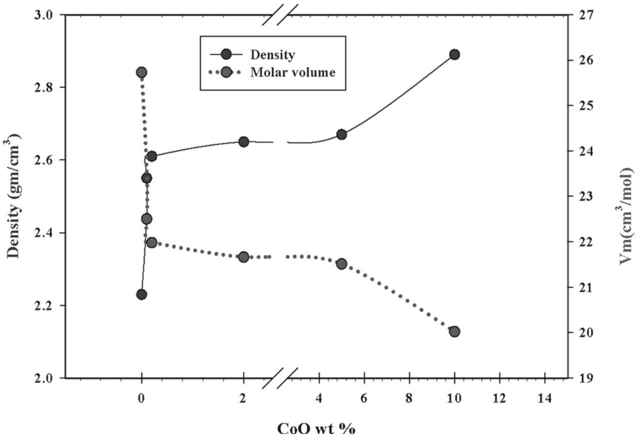


Fig. 1 Density (ρ) dependence on glass composition and molar volume (V_m) for lithium borate glasses undoped and doped with varying CoO content

2 Experimental

2.1 Preparation of the Glasses

Lithium borate glasses were prepared from chemical grade powder. Boric oxide was introduced in the form of orthoboric acid and lithium oxide was introduced in the form of its anhydrous carbonate. Cobalt oxide was added in the form of pure CoO. Compositions of the studied glasses are shown in Table 1. The batches were melted in porcelain crucibles at 1150^{o}C±20^{o}C for two hours in an electrically heated furnace and each melt was stirred by rotating the crucible several times every 30 min. The homogeneous melts were cast after two hours of melting into preheated stainless steel molds. Then the prepared samples were immediately transferred to an annealing furnace regulated at 350 ^{o}C±50^{o}C. The muffle after one hour was left to cool to room temperature at a rate of 25^{o}C/h.

2.2 Density and Molar Volume

Density was measured at room temperature, using the suspended weight method based on Archimedes principle. Xylene was used as the immersion liquid. All the measurements were repeated three times. Density was calculated according to the following formula:

$$\rho = [a/(a - b)] \text{ x } 0.86$$

Where ρ is the density of the glass sample, a and b are the weight of the glass sample in the air and xylene respectively, and 0.86 is the density of xylene at 20^{o}C. The relationship between density and composition of an oxide glass system can be expressed in terms of an apparent volume V_m occupied by 1g atom of oxygen. The molar volume, V_m of all

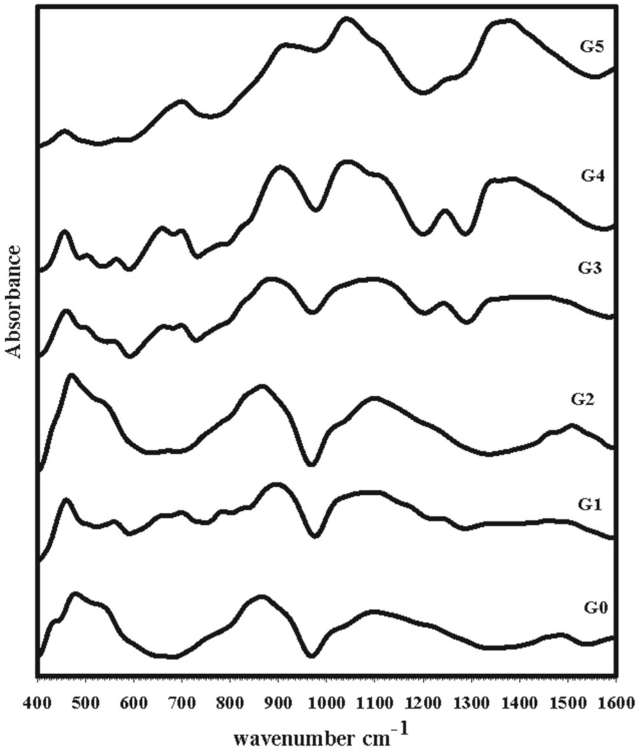


Fig. 2 IR spectra of base $Li_2O - B_2O_3$ glasses undoped and doped with varying CoO content

the prepared glasses, defined as the mean molecular weight M of glass constituents divided by its experimental density is given in the following equation:

$$V_m = M/\rho$$

2.3 Infrared Absorption Spectra Measurements

The FTIR absorption spectra were obtained at room temperature using a JASCO FTIR 6200 spectrometer. IR absorption spectra were measured immediately after preparing the disks of KBr and glass samples. The FTIR spectra were recorded in the wavenumber range of 400-4000 cm^{-1}. A quantitative analysis of the infrared spectrum has been carried out by a careful deconvolution of the absorption profiles utilizing the “peak fit” program. IR spectra were corrected for the dark current noises and background using a two-point base line correction. Many trials have been carried out using different band shapes but best fit obtained was found to be the Gaussian shape. The position of each band, its width and intensity are parameters adjustable automatically by the program, on the basis of the minimization of the deviations between the experimental and simulated spectrum.

2.4 Irradiation Facility

Glasses were subjected to doses of 50 and 200 kGy using an Indian ^{60}Co gamma-rays cell (2000 Ci) with a dose rate 2.08 kGy/ h. The samples were placed in a manner that each glass sample was subjected to the same irradiation dose.

3 Results and Discussion:

3.1 Density and Molar Volume Results

The density is a powerful tool for exploring changes in the structure of glasses. Density is affected by the structural softening/ compactness, change in geometrical configuration, coordination number, cross-link density and dimension of interstitial spaces of the glass. From Fig. 1, the density of the studied glasses increases with the increase of CoO content, while the molar volume decreases over all the studied glass samples. Since density is weight /volume then if an added component has a high molecular weight this will cause an increase in the glass density if the volume is not affected by this addition. The observed large increase in the glass density when CoO is added to glass up to 2 wt% can be attributed to its high molecular weight 74.93 g mol^{-1}[14, 15].This addition will cause an increase in weight without any increase in the glass volume assuming that Co^{2+} ions will occupy the glass vacancies along with Li^{+}ions and act as a glass modifier. This will be followed by a slight increase in density when the CoO content increases to 2- 5 wt% CoO assuming that this amount will be more than that required to fill vacancies. These will then be assumed to occupy the substituent positions causing an expansion in the volume to be able to house itself in this space. When the Co content increases from 5-10 wt% it may act as a glass former causing an increase in density.

Table 2 Positions of IR absorption bands of all studied glasses

Peak positions (cm^{-1})	IR assignments(References)
420-470 cm^{-1}	Specific vibrations of Li-O bonds(18)
500–550 cm^{-1}	The borate deformation modes(19)
780–1100 cm^{-1}	The B–O symmetric stretching of tetrahedral BO_4 units and vibrations of diborates bridging to pentaborate groups(20)
1420–1540 cm^{-1}	Anti- symmetrical stretching vibrations with three NBOs of B–O–B groups(21)
1320 cm^{-1}	Asymmetric stretching relaxation of B-O bond of trigonal BO_3 units with (NBOs) (22,23)

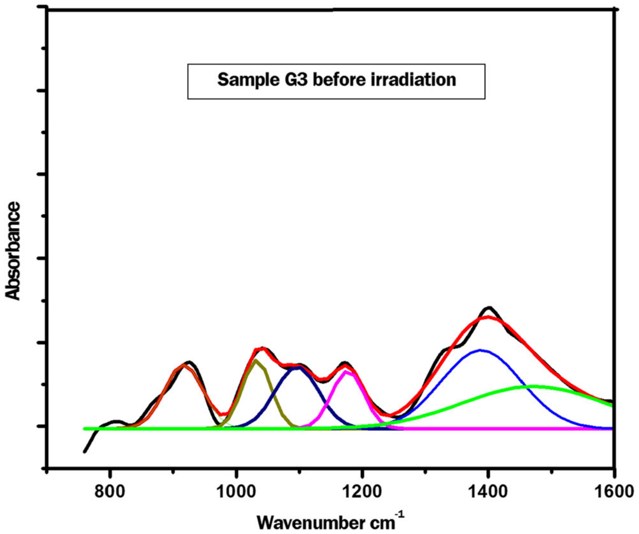


Fig. 3 Example of deconvolution of IR spectra for G3 glass before gamma irradiation

3.2 FTIR Analysis

3.2.1 Effect of Composition

The IR spectra of lithium borate glass (LBG) and those doped with different concentrations of CoO were investigated as shown in (Fig. 2). In this study, it was observed that the vibrational modes of the borate network are mainly active in three infrared spectral regions from 1200 to 1500 cm^{-1} (B– O stretching of trigonal BO$_3$units), from 800 to 1200 cm^{-1} (B–O stretching of tetrahedral BO$_4$ units) and from 600 to 800 cm^{-1} (bending vibrations of various borate segments).

These bands are shifted under the influence of the surrounding cations, the extent and direction of the shift depending on the type of the cation. In pure B$_2$O$_3$ glass, 806 cm^{-1} is a characteristic frequency of the boroxol ring. The absence of this absorption band in the present case means that the boroxol ring in the glass structure is substituted by BO$_3$ and BO$_4$ groups [16].

Careful comparison of such spectra and their trails following different proportions, based on information predicted from previous studies leads to the following assignments shown in Table 2. Figure 2 shows that the FTIR spectra of G0 consist of three small bands at 440, 470 and 550 cm^{-1}. There is a distinct prominent band at 870 cm^{-1}, a medium broad band at 1100 cm^{-1} and a small kink at about 1460 cm^{-1}. The band at 440 cm^{-1}, corresponding to the region 420-470cm^{-1}, is assigned to specific vibrations of Li-O bonds [17]. The band centered at 550 cm^{-1} in the region 500–550 cm^{-1} is assigned to the borate deformation modes [18], the band at 870 cm^{-1} assigned to the spectral band in the region 780–1100 cm^{-1} is due to the B–O symmetric stretching of tetrahedral BO$_4$ units and vibrations of diborates bridging to pentaborate groups [19]. The band at 1100 cm^{-1} may be due to a stretching vibration of B-O bonds in BO$_4$ units from tri, tetra, and penta borate groups and the band at 1460 cm^{-1} assigned to the spectral band in the region 1420–1540 cm^{-1} is attributed to anti-symmetrical stretching vibrations with three NBOs of B–O–B groups [20]. Figure 2 also shows the FTIR of samples containing progressive additions of CoO.

Evidently the main IR spectral vibrations are generally persistent but some changes are observed with doping CoO where G1 shows a marked decrease in the intensity of bands.

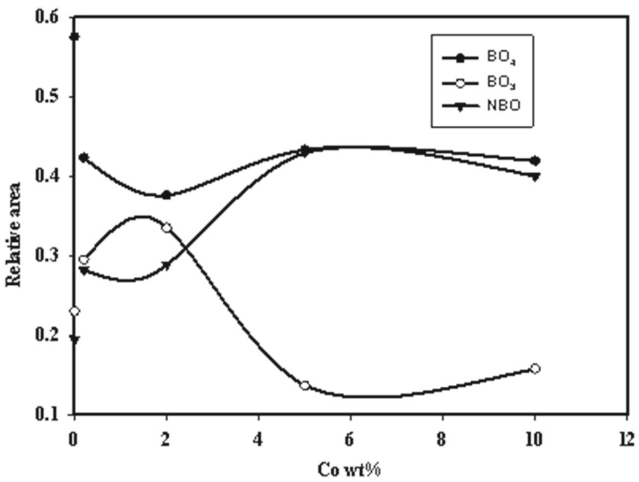


Fig. 4 The effect of CoO content on composition as a function of BO$_3$, BO$_4$ and NBOs of the studied glass samples before gamma irradiation

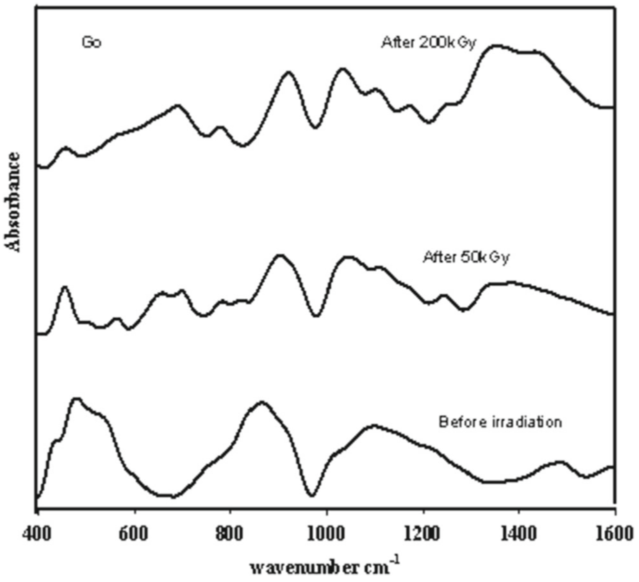


Fig. 5 IR spectra of G0 glass before and after irradiation dose 50 and 200 kGy

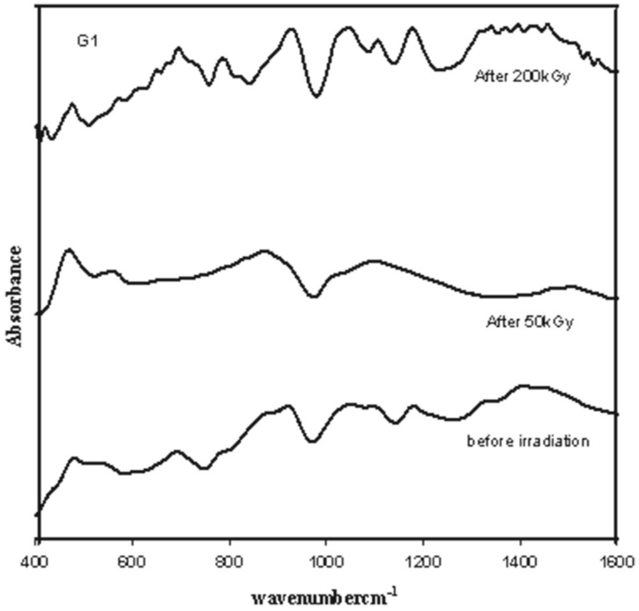


Fig. 6 IR spectra of G1 glass before and after irradiation dose 50 and 200 kGy

Also new weak bands appeared at, 780, 860, 920 cm^{-1} as mentioned before related to the B–O symmetric stretching of tetrahedral BO_4 units and vibrations of diborates bridging to pentaborate groups. The band at 1320 cm^{-1} is due to asymmetric stretching relaxation of B-O bonds of trigonal BO_3 units with NBOs [21, 22].

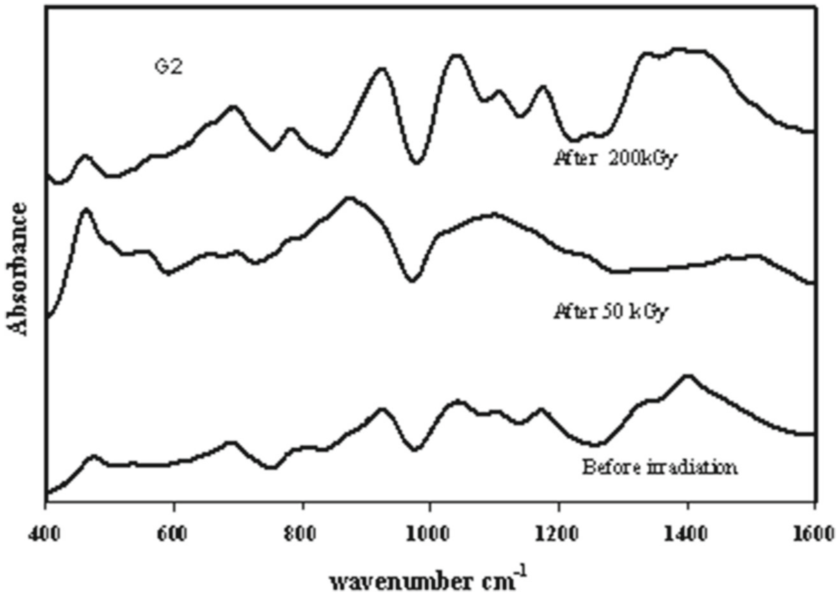
Further insertion of CoO in sample G2 shows an increase in the band intensities, especially the bands at 470, 680, 870, 1100, 1320 and 1460 cm^{-1}. While the band at 870 cm^{-1}was shifted to 925 cm^{-1}, the medium broad band at 1100 cm^{-1} was shifted to 1040cm^{-1}, and the band at 1460cm^{-1}was shifted to 1370 cm^{-1}. This suggests that some bands of BO_4 groups shifted to higher wavenumber, while the BO_3 groups shifted to a lower wavenumber which is in agreement with other researches [20, 23].

Therefore, the network of this glass would be modified by the presence of CoO, where the association of alkali oxides with both CoO and B_2O_3 affects the borate structure. Therefore, the BO_4 units will be destroyed and converted into asymmetric BO_3 units with NBOs, is in agreement with other researches [20, 24]. It is difficult to extract new information about the modifications of the glassy matrix, except that reported in the literature, which depends on the type and/or content of the alkali oxide in borate glasses. Therefore, the deconvolution method is used for analyzing the infrared spectra of borate glasses to determine the concentration of borate structural units.

Figure 3 shows the deconvolution of sample G3 extracted from the IR spectra. The relative area of each band is proportional to the concentration of borate structural groups corresponding to a particular band. According to Fig. 3 the decrease in the area under the bands around 800-1200 cm^{-1} for glasses with low content of CoO up to 2 wt%, can indicate a decrease in the formation of BO_4 units.

This assumption can be ascertained by Fig. 4 where there is an increase in the amount of both BO_3 and NBO, while, BO_4 decreases. This observation can be attributed to the conversion of BO_4 to BO_3 and NBO as a result of the formation of CoO_6, which requires an additional amount of oxygen atoms, this result is in agreement with Gaafar et al. [20]. However by further increase in CoO content more than 2 wt% the formation of BO_4 units increases on account of the BO_3 units as shown in Fig. 4. This can be attributed to

Fig. 7 IR spectra of G2 glass before and after irradiation dose 50 and 200 kGy



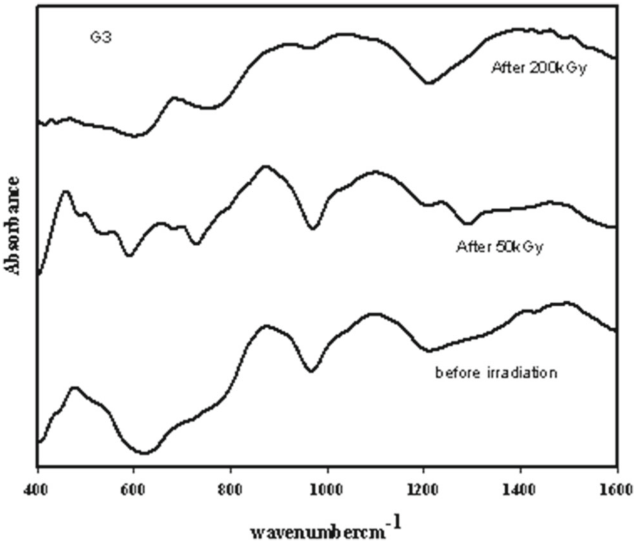


Fig. 8 IR spectra of G3 glass before and after irradiation dose 50 and 200 kGy

the formation of covalent Co-O-B bonds which is in agreement with Rajyasree et al. [23] which produce the a shoulder band at 680 cm^{-1} in Fig. 2. The observed increase in the intensity of the band at 680 cm^{-1} which can be noticed in Fig. 2 with the increase of CoO content from 5-10 wt% gives a good indication that the Co^{2+} ions started to act as a network former [16].This conclusion is also in agreement with the density results.

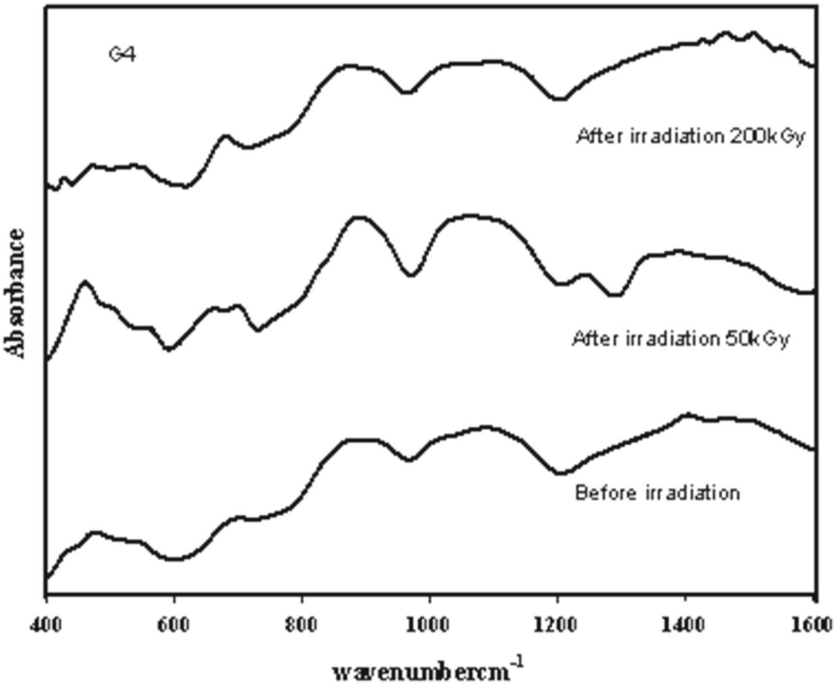
3.2.2 *Effect of Irradiation*

Knowledge of the glass structure before and after gamma irradiation is a prerequisite for understanding the structural evolution of glasses, and deconvolution of IR spectra to calculate BO_4 values for borate glasses. The IR spectra after irradiation reveal the main spectral features of the borate network as observed in the original samples. However, some changes in terms of increase or decrease in the intensity of bands or shifting of bands either to lower or higher wave numbers are observed [16].

Figure 5 shows the IR spectrum of glass sample G0. This composition is affected by gamma irradiation at a dose of 50 kGy before and after irradiation with 50 and 200 kGy respectively. From that figure, it can be seen that before irradiation the region from 800 -1200 cm^{-1}which is related to BO_4 and the region from 1200-1400 cm^{-1} which is related to BO_3, changes after exposure to 50 kGy. The intensity of some bands decreases followed by the appearance of some new weak bands as the BO_4 is transformed into BO_3 triangles with non-bridging oxygens. By increasing the radiation dose at 200 kGy, the relative area which represents BO_4 decreases. However, the area under the peaks, which is related to BO_3 triangles with NBOs in the region 1200-1400cm^{-1}, increases which shows that the G0 sample is affected by radiation at both 50 and 200 kGy.

With addition at 0.1 wt% G1 CoO glass, Fig. 6 shows the FTIR spectrum of G1 before and after an irradiation with 50 and 200 kGy. The figure shows after irradiation dose of

Fig. 9 IR spectra of G4 glass before and after irradiation dose 50 and 200 kGy



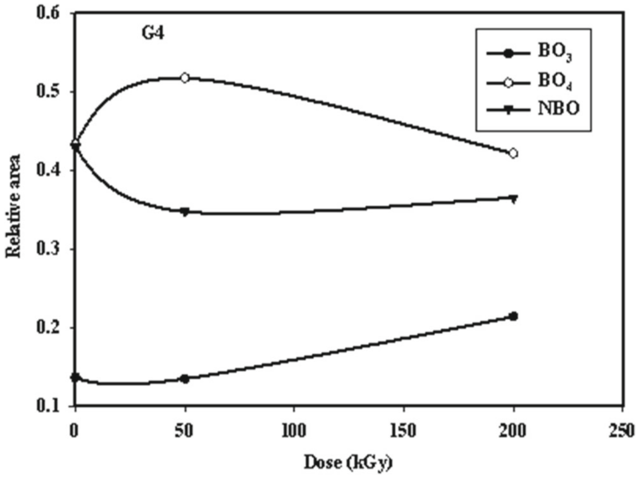


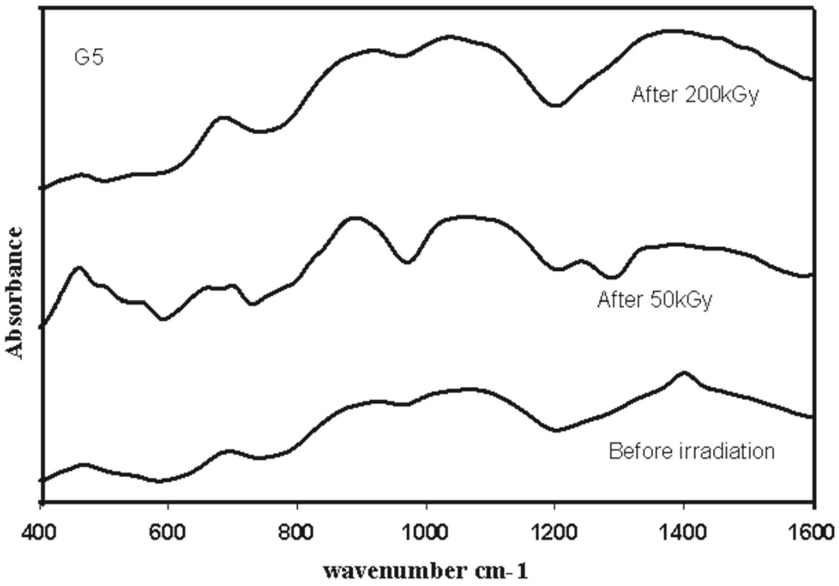
Fig. 10 The effect of gamma irradiation dose as a function of BO_3, BO_4 and NBOs for G4 glass

50 kGy that the relative area of the bands related to BO_4 is greater than that of BO_3 and many bands disappear. However, at 200 kGy a large number of bands appear; it can be assumed that gamma irradiation causes structural disorder and this leads to change in the bond position and/or the bond angle of the building units.

Radiation induced damage generated in glasses depends on the dose of radiation, the type and composition of the glasses, and the intrinsic defects within them [13]. From Fig. 7 it can be seen that G2 is affected by γ- radiation in the same way as G1. From the IR spectra of glass sample G3, with content 2 wt% CoO a slight change is observed when irradiated with 50 kGy as shown in Fig. 8. At a higher dose of 200 kGy the broad band lying in the region 800-1150 cm^{-1} widens which indicates that radiation causes disruption of the structure and this broading of the bands makes it clear that the basic glass forming units of BO_3 and BO_4 retain their position and changes only occur in the bond angles. In sample G4 with content 5 wt% CoO a slight change is observed when irradiated with 50 kGy as shown in Fig. 9, while at 200 kGy the positions of different bands with respect to those of pre-irradiation do not change, which suggests that main building units remain in the same position. Sample G4 acts as a glass former, which can be considered as radiation resistant and this can also be ascertained from the deconvolution data obtained from the deconvolution of the IR spectrum of G4 before and after irradiation as shown in Fig. 10. After irradiation it is probable that a large portion of the unstable induced defect centers decrease or bleach out.

Another postulate is structural rearrangement which includes release of positive holes to be combined with electrons and hence bleaching of induced defects. From these observations, we can conclude that glass sample G4 containing 5 wt% CoO content is relatively resistant to gamma irradiation at 200 kGy, Fig. 10 shows the values of BO_4, BO_3 and NBOs obtained from the deconvolution of IR spectra of glass sample G4 as a function of irradiated dose where the change in three parameters is too small to be detected as has been concluded from Ehrst and Vogel [12]. The concentration of each vibrational mode is considered to be proportional to the relative area of its characteristic component band. When, the content of CoO increases

Fig. 11 IR spectra of G5 glass before and after irradiation dose 50 and 200 kGy



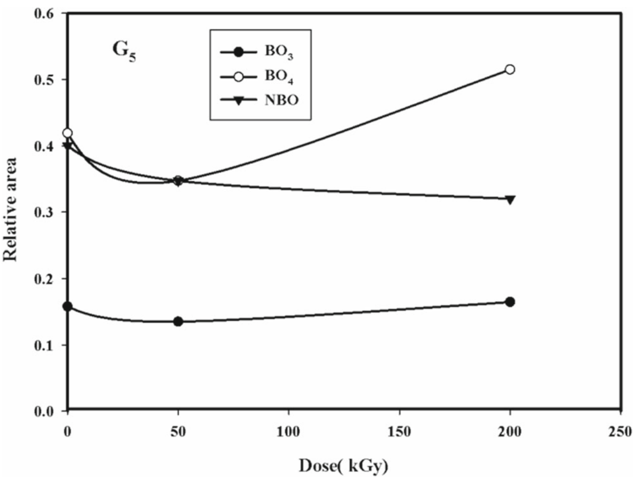


Fig. 12 The effect of gamma irradiation dose as a function of BO_3, BO_4 and NBOs for G5 glass

to 10 wt% in glass sample G5 as shown in Fig. 11 after its exposure to gamma irradiation at 50 kGy, it is found that the G5 sample is slightly affected by gamma radiation at 50 kGy. However, the observed spectra at 200 kGy is not obviously changed. The deconvolution of the IR spectra of sample G5 from Fig. 12, shows that there are changes in BO_4, BO_3 and NBOs which may be due to the interaction with gamma irradiation and these change are more than that of sample G4 in agreement with Mansour et al. [14].

From these observations it is concluded that the glasses doped with 5 wt% of CoO are relatively more resistant to the radiation when compared with the other studied samples.

4 Conclusion

From this study it may be concluded that:

- The density of the studied samples increases as CoO content increases.
- Infrared absorption spectra of the glasses indicate the presence of both triangular and tetrahedral borate units besides formation of B-O-Co bonds in the glass network.
- Infrared absorption spectra show that at low concentration of CoO up to 2 wt% cobalt ions play the role of network modifier in the form of six fold coordination CoO_6, which requires more oxygen and so it converts BO_4 into BO_3 with NBOs. At more than 2 wt% the cobalt ions play the role of network former, in the form of CoO_4; it requires less oxygen and so BO_4 increases with increasing CoO which increases the connectivity.
- Gamma irradiation results in the transformation of the tetrahedral BO_4 group to the triangular BO_3 one along with non-bridging oxygens. At 5 wt% of CoO, the Co ions may enter the glass network through B-O-Co bonding, making the glass more resistant to the effect of gamma radiation when compared with the other studied samples.

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