



# Spectroscopic Studies and the Effect of Radiation of Alkali Borate Glasses Containing Chromium Ions

A.I. Ismail<sup>a</sup>, A. Samir<sup>b,\*</sup>, F. Ahmad<sup>c,\*</sup>, L.I. Soliman<sup>d</sup>, A. Abdelghany<sup>c</sup>

<sup>a</sup> Physics Department, Modern Academy for Engineering and Technology in Maadi, Cairo, Egypt

<sup>b</sup> Engineering Mathematics and Physics Department, Faculty of Engineering at Shoubra, Benha University, 11629, Cairo, Egypt

<sup>c</sup> Physics Department, Faculty of Science, Al-Azhar University (Girls Branch), 11754, Cairo, Egypt

<sup>d</sup> National Research Centre, Dokki, 12622, Cairo, Egypt

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## ABSTRACT

The glassy system under investigation is  $y \text{Li}_2\text{O} - 25 \text{ZnO} - 49.9 \text{B}_2\text{O}_3 - (25-y) \text{Na}_2\text{O} - 0.1 \text{Cr}_2\text{O}_3$ , where  $y = 0, 10, 20, 25$  mol%, and it was prepared via traditional melt quenching technique. The optical absorption spectrum of alkali borate glass containing Cr ions reveals a decrease in  $\text{Cr}^{6+}$  contributions as the lithium content increases. The strength of crystal field decreases, while the value of both Racah parameters B and C clearly follow a reverse behavior as the content of  $\text{Li}_2\text{O}$  increases. The chromium ion has a more ionic environment, and larger numbers of electrons are localized on the d-shell. The obtained ESR signals pointed out the presence of both  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  states in the host borate glass. FTIR spectra indicated the existence of some bonds, denoting B-O bonds vibrations from  $\text{BO}_3$  as well as  $\text{BO}_4$  units. An estimation of the fraction  $N_4$  has been conducted, utilizing the characteristic parameters of IR. Glass samples were influenced by  $\gamma$ -Irradiation, and a minor change occurred in bond angles and lengths of the structural units of borate. This proves the minor diversity of the IR bands intensity.

## 1. Introduction

Borate glass is one of the most important glass forms known. It is often suitable, optical and dielectric. Besides, it insulates materials that are highly transparent, have a low melting point and have a high thermal stability. It can also be utilized in many applications [1,2]. Borate glasses reveal a diversity of structural alterations with alkali content, and they provide a propitious host for incorporating  $\text{Cr}^{3+}$  ions [3,4]. Upon the addition of alkali modifier ions to  $\text{B}_2\text{O}_3$  glass, some of the  $\text{BO}_3$  units present as boroxal rings turn into the  $\text{BO}_4$  units for specific limit of modifiers. After that limit, non-bridging oxygen are composed upon the increase of the modifier oxide [5,6]. Great efforts have been exerted to develop novel glassy materials, through either doping or adding transition metal ions (TMI). Studying glasses new properties is greatly pertinent, since they are potentially applicable in diverse fields of technology [7,8]. Amongst the various transition metal ions, chromium is one of the most researched (examined) TM ions (being a low-cost activator). Besides, chromium is a paramagnetic ion: upon dissolving in glass matrices, even in very little amounts, chromium colors the glasses, and it greatly influences the glasses optical properties. Thereby,

$\text{Cr}^{3+}$  ions provide a helpful examination for obtaining information about the glasses' amorphous local environment [9]. Upon being subjected to ionizing radiation ( $\gamma$ -rays), glasses may become dark due to the occurrence of defects or damages [10,11]. Presumably, such induced variations are a result of interacting of free electrons, ensuing positive holes generated with the substantial flaws that are already found in the glasses prior to irradiation, or the impact of electrons and positive holes found on the traces of impurities that contaminate the glasses. It is possible to identify the formed induced defects through optical or ESR measurements [11,12]. Electron spin resonance (ESR) confirmed the presence of  $\text{Cr}^{6+}$ , via identifying the state of its charge transfer (i.e.,  $\text{Cr}^{5+} \text{O}^-$ ), and  $\text{Cr}^{3+}$ , whilst infrared spectroscopy supplied the glasses' local structure [13-15]. Spectroscopic techniques, like optical absorption, ESR and IR, are the most convenient experimental techniques among the diverse sampling methods for studying the structural information of glass. Alkali borate glasses are an ideal case when compared to other glass forming systems for demonstrating the effectiveness of the spectroscopic techniques in the science of glass [16]. Lots of authors have noted that several heavy metal oxides that contain glasses or transition metal ions reveal shielding behavior towards  $\gamma$  irradiation, whereas their optical

\* Corresponding authors.

E-mail addresses: [ahmed.soliman01@feng.bu.edu.eg](mailto:ahmed.soliman01@feng.bu.edu.eg) (A. Samir), [fatma.ahmed@azhar.edu.eg](mailto:fatma.ahmed@azhar.edu.eg) (F. Ahmad).

and FTIR spectra stay almost stable with the persistent  $\gamma$  irradiation [17, 18].

The present study aims to show the effect of  $\gamma$ -irradiation on ligand field parameter, ESR and FTIR absorption spectrum as a function of  $\text{Li}_2\text{O}$  content for borate glasses doped with 0.1 $\text{Cr}_2\text{O}_3$  mol%.

## 2. Experimental details

### 2.1. The preparation of samples

Alkali borate glass system that is composed of  $y \text{Li}_2\text{O} - 25 \text{ZnO} - 49.9 \text{B}_2\text{O}_3 - (25-y) \text{Na}_2\text{O} - 0.1\text{Cr}_2\text{O}_3$  is prepared;  $y = 0, 10, 20, 25$  mol% were produced via melt-quenching method. The starting materials were  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$  powders. To prepare this composition, stoichiometric quantities of the precursors were weighed and fully mixed in a mortar for guaranteeing adequate homogeneities. Then the mixture was melted at 1000 °C for  $\sim 45$  min in an electric muffle furnace. The melt was speedily poured, and two copper plates were used to press it, producing glass flakes with minimum thickness. An agate mortar was used to grind the glass pieces to obtain fine powders for ESR and FTIR measurements.

### 2.2. Samples characterization

X-ray diffraction (XRD) measurements are taken utilizing (Phillips-PW3719) diffractometer with  $\text{Cu-K}\alpha$  X-ray beam that has a wave length of 1.542 Å. X-ray diffraction patterns were recorded in  $2\theta$ , ranging between 4 and 80° with a scanning rate of 2°/min. Optical measurements were recorded over the wavelength range of 200–1000 nm, utilizing JenWay-6405 UV-VIS spectrophotometer. Before conducting optical studies, all samples were finely polished. A record of ESR spectra was taken utilizing X-band EMX spectrometer (Bruker Germany) on the powder samples that are put into standard quartz tubes. The field modulation was set to 100 kHz, and the microwave power was set to 10 mW, whereas the magnetic field was scanned in the range of 75–5000 G. The FTIR absorption was gained via KBr pellets technique in the range of 1600–400  $\text{cm}^{-1}$ , utilizing (FT-IR Perkin Elmer). The entire measurements have been accomplished at surrounding conditions on the as-quenched samples. A source of  $^{60}\text{Co}$  gamma (Gamma chamber 4000 A, produced by Atomic Energy Agency of Egypt) was utilized to perform irradiation of the glass samples. The glass samples were irradiated (dose

rate 2 and 4 Mrad) for the requisite interval of time for achieving the required total dose  $\sim 24$  h.

## 3. Results and discussion

### 3.1. X-Ray diffraction

X-Ray diffraction was utilized to check the obtained glass samples. Fig. 1 shows the X-ray spectra of the prepared glasses in the powder form. The diffraction charts demonstrate no sharp peaks, and that indicates the prepared samples non-crystalline nature. The featureless X-ray spectra intensity has a similar order to the entire samples, and that indicates the same degree of the prepared samples amorphousity [19]. Additionally, the patterns reveal a broad hump at ( $2\theta \sim 30^\circ$ ), and this is a typical property of borate glasses [20].

### 3.2. UV-Vis. Spectroscopy

The optical absorption spectra of the glasses before and after irradiation is shown in Fig. 2. It is noted that the absorption edge is not sharp, which asserts that the prepared compositions are glassy in nature, and is in accordance with the XRD measurements. After irradiation there is no disappeared or new band related to some shielding effect of Cr ions where it causes the blocking of the free transit or transfer of the loosed electrons during the irradiation process. The slight increase in absorption bands intensity of irradiated samples could have resulted from photochemical reactions between the 3d Cr ions [21–23]. During irradiation, electrons and/or positive holes are produced by  $\gamma$  irradiation. It is possible that Cr ions would absorb the excited electrons or pick up the liberated holes, they are subsequently altered to lower or higher valence states ( $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ ), respectively. Thereby, they share in the shielding process [24–26]. Discrete Cr transition chiefly dominates the absorption spectra for all samples. Specifically, the absorption bands in the UV/visible range are an indication of the existence of  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$ , respectively, with the sample glass host. In contrast, the researches of optical absorption glasses that are doped in transition metals result in the ligand field of energies of absorption, which, in turn, indicate the octahedral and tetrahedral coordination distortion. The samples spectrum demonstrates two main absorption bands at  $\sim 605$  ( $\nu_1$ ) and 420 ( $\nu_2$ ) nm; that can be determined according to the normal transitions of  $\text{Cr}^{3+}$  ions [7,21]. The spectra have been analyzed and the bands have

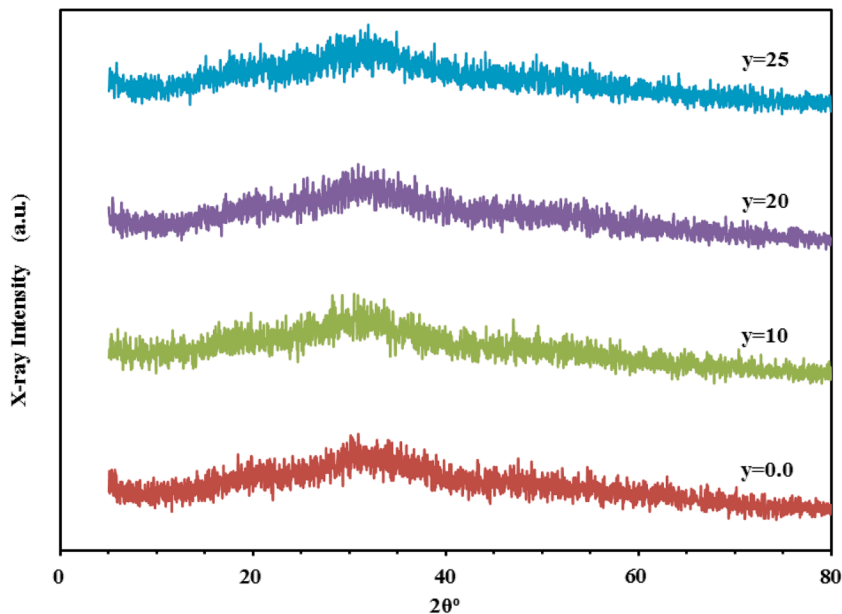


Fig. 1. XRD pattern of the investigated samples.

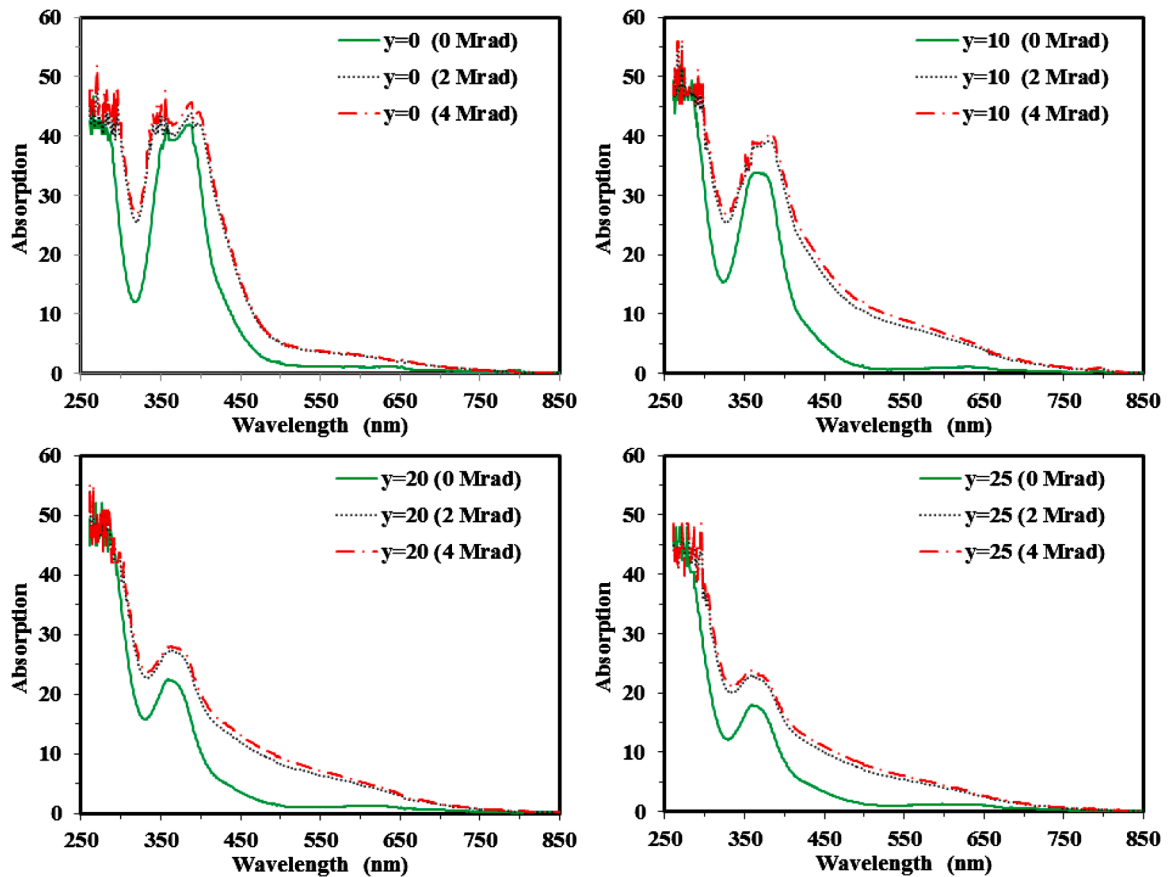


Fig. 2. Optical absorption spectra of the investigated samples before and after irradiation.

also been assigned to  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  transitions respectively, and this, in turn, refers to d-d transition of  $Cr^{3+}$  ion. The color of the samples that are prepared is yellow green, and this indicates a trivalent chromium oxidation state [3]. Moreover, it is possible to identify  $Cr^{6+}$  ion by the absorption of the charge transfer in the UV range around  $\sim 370$  and  $350$  nm, which is attributed to the transition of  ${}^4A_{2g} \rightarrow {}^2A_{1g}$  and  ${}^4A_{2g} \rightarrow {}^2T_{1g}$  (P), respectively. ( $v_3$ ) represents the average sum of the chromium hexavalent bands position. The cause of this is most probably the contribution of the chromium ions in a state of higher valency ( $Cr^{6+}$ ), which is not d-d transition [13,15]. The spectra showed a limited shift of the position of absorption bands after irradiation. The thorough UV range absorption is an indication that it is not d-d absorption. That absorption could possibly be related to the existence of Cr ions in a state of higher valency, possibly as  $Cr^{5+}$  and/or  $Cr^{6+}$  ions [27-31].

Obviously, a decrease in the intensity of absorption bands of  $Cr^{6+}$  occurs as the content of  $Li_2O$  increases. This is possibly attributed to the decrease of optical basicity of the matrix glass with increasing  $Li_2O$  content ( $Li < Na$ ). This is an indication of a decrease in the content of  $Cr^{6+}$  ions and the reduction of a portion of the chromium to a lower valence [30,32].

A calculation of the ligand field parameters, as crystal field strength ( $10Dq$ ), which represents the crystal field splitting energy and the Racah parameters, ( $B$  and  $C$ ) which provides a measurement of the interelectronic repulsion within the 3d electrons of chromium ion, were conducted from the spectral band absorption positions ( $v_1, v_2, v_3$  in  $cm^{-1}$ ). This calculation has been performed using the relations [33]:

$$10Dq = v_1 \quad (1)$$

$$B = \frac{(2v_1 - v_2)(v_2 - v_1)}{(27v_1 - 15v_2)} \quad (2)$$

$$C = \frac{v_3 - 4B - v_1}{3} \quad (3)$$

Fig. 3 shows the ligand field parameters values ( $Dq$ ,  $B$ ,  $C$  and  $Dq/B$ ) obtained before and after irradiation. Clearly, the crystal field  $Dq$  decreases as  $Li_2O$  content increases. On the other hand, the Racah parameters  $B$  and  $C$  values clearly follow an opposite trend. These results are an indication of strong electron localization at  $Cr^{3+}$  ions. Hence, the inter electronic repulsion in the d-shell turns relatively intenser, leading to the existence of chemical bonds between  $Cr^{3+}$  ions and the ligands with a more ionic character [9,19,34]. Crystal field strength is described by the ratio  $Dq/B$ . It was found that the value of  $Dq/B$  exceeded 2.3 in the strong crystal field sites, and it was much less than 2.3 in the weak field, and it was close to 2.3 in the intermediate fields [3]. Table 1 shows that the relation between Racah parameters ( $C/B$  ratio), namely  $C = 4B$ , is acceptably satisfied (i.e.,  $C = 3.5B \pm 0.2$ ). Moreover, the degree of ionicity of the ligand bonding is defined utilizing the Racah parameters. The formation of the bonding (or nephelauxetic ratio  $h$ ) has also been estimated utilizing the next formula [20]:

$$h = \frac{[(B_{free} - B)/B_{free}]}{K_{Cr^{3+}}} \quad (4)$$

where  $B_{free} = 918 \text{ cm}^{-1}$  is the value of the free (gaseous)  $Cr^{3+}$  ion, and the central metal ion is  $K_{Cr^{3+}} = 0.211$ . The appointed values of  $h$  parameter decrease with lithium oxide content, indicating the increase in the ionic bonding nature between Cr ions and the surrounding ligands and the increased localization of 3d electrons [9,13,19,34]. The obtained values of  $h$  for all the investigated glasses before and after radiation show the same behavior as  $Dq$  (Table 1). From the spectra in Fig. 2, it is clear that the absorption edge shifted towards higher wavelength with increasing of  $Li_2O$  content. The optical band gap energy values  $E_g$

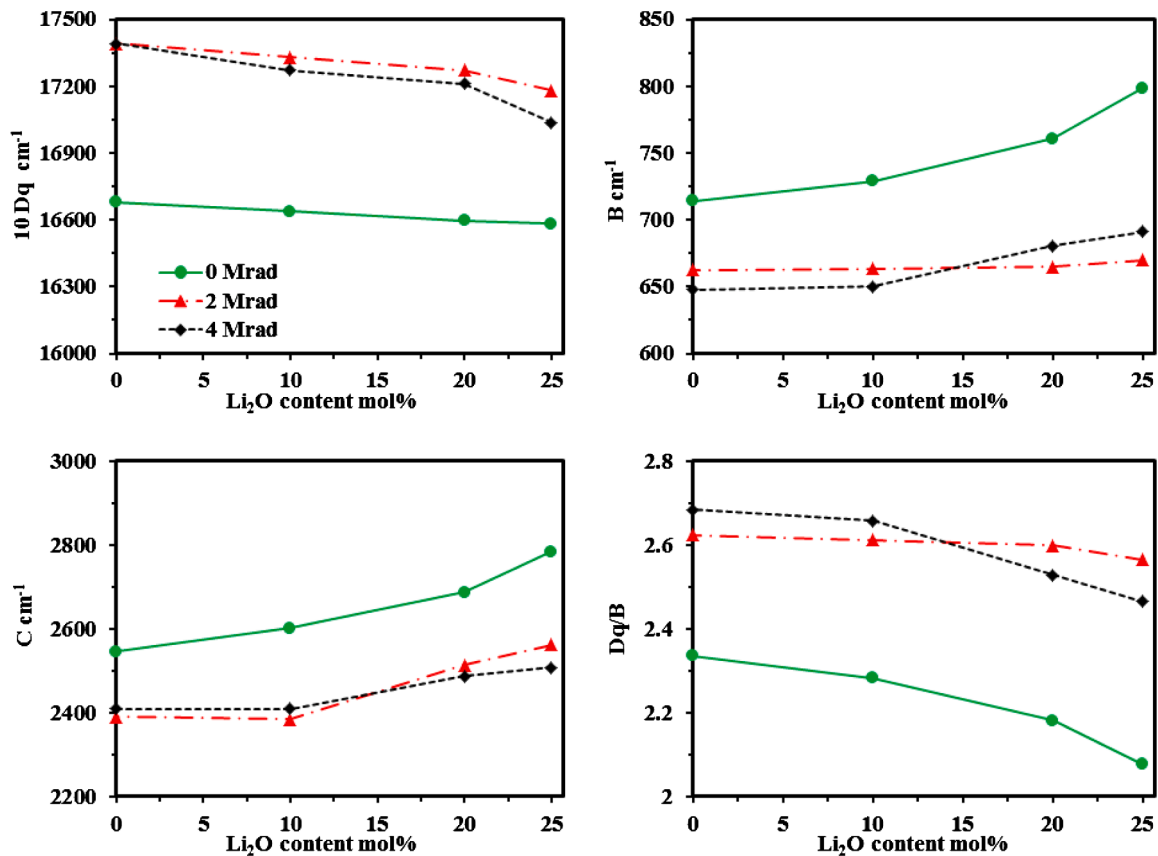


Fig. 3. The ligand field parameters values ( $Dq$ ,  $B$ ,  $C$  and  $Dq/B$ ) before and after irradiation as a function of  $Li_2O$  content.

Table 1

C/B, nephelauxetic ratio  $h$ ,  $E_g$  and  $E_t$  values of Li doped borate glasses containing 0.1  $Cr_2O_3$  mol.% at different  $\gamma$  radiation doses.

$y$ mol. %	C/B			$h$			$E_g$ (eV)			$E_t$ (eV)		
	0 Mrad	2 Mrad	4 Mrad	0 Mrad	2 Mrad	4 Mrad	0 Mrad	2 Mrad	4 Mrad	0 Mrad	2 Mrad	4 Mrad
0	3.56	3.61	3.72	1.06	1.32	1.40	3.59	3.05	2.92	0.28	0.33	0.38
10	3.57	3.59	3.71	0.98	1.32	1.39	3.43	2.97	2.88	0.44	0.56	0.61
20	3.53	3.78	3.65	0.82	1.31	1.23	3.39	2.94	2.79	0.46	0.63	0.69
25	3.48	3.82	3.63	0.62	1.29	1.18	3.37	2.89	2.69	0.48	0.67	0.72

were obtained via the following equation [13,35,36]:

$$ah\nu = A(h\nu - E_g)^n \quad (5)$$

where  $n = 2$  for indirect allowed band transition model for the glassy samples. It could be noted from the plots of  $(\alpha h\nu)^{1/2}$  as a function of photon energy  $h\nu$  that the values of  $E_g$  obtained before and after radiation (demonstrated in Table 1), decrease upon the increase of the content of  $Li_2O$ .

It is possible to evaluate the Urbach energy  $E_t$  from the relation [35, 36]:

$$\alpha(\omega) = \alpha_0 \exp(h\nu / E_t) \quad (6)$$

To characterize the degree of disorder in glassy systems as dangling bonds and non-bridging oxygen NBO, Urbach energy is utilized. An increase occurs in the  $E_t$  values of the present samples (Table 1). It is observed that as the content of  $Li_2O$  increases, an increase occurs in the optical band gap energy  $E_g$ , and an increase in Urbach energy takes place. This is possibly the result of lithium ions that causes a structural change in the glass network. The NBO formation which bind excited electrons less tightly than bridge oxygen increases with further adding of  $Li_2O$  and break up the standard structure of the borate as a result the

band gap decreases [37,38]. Urbach energy increases because of the increase in the degree of disorder in glass structure upon the increase of the content of  $Li_2O$ , which accords with FTIR measurements as inferred later. Materials that have more Urbach energy greatly tend to transform weak bonds into defects [39].

### 3.3. ESR spectroscopy

ESR spectra for the investigated glass system before and after radiation dose are represented in Fig. 4 (4 Mrad). The spectra have been normalized according to mass for conducting a proper comparison between various samples. The spectra of ESR exhibit a considerable dependence on the alkali oxide contents. ESR spectra featuring two resonance signals at a low magnetic field with effective  $g$  estimates at  $g = 4.82$  are probably related to isolated  $Cr^{3+}$  ions in strong ligand field sites [6,8,15, 30,34,40]. The second signal at  $g = 4.11$  is generally an attribute of  $Cr^{3+}$  ions, despite the fact that  $Fe^{3+}$  impurities are possibly at the origin of this signal [1,7,30,34,41,42]. At high field, ESR spectra reveal two resonances with effective  $g$  values at 2.21 and 1.93. The signal at  $g = 2.21$  is attributed to exchanging the coupled pairs, it could be attributed to the existence of large  $Cr^{3+}$  clusters [14,34,41]. Furthermore, the signal observed at  $g = 1.93$  was because of  $Cr^{5+}$  ions ( $Cr^{5+}$  equivalent to  $Cr^{6+}$

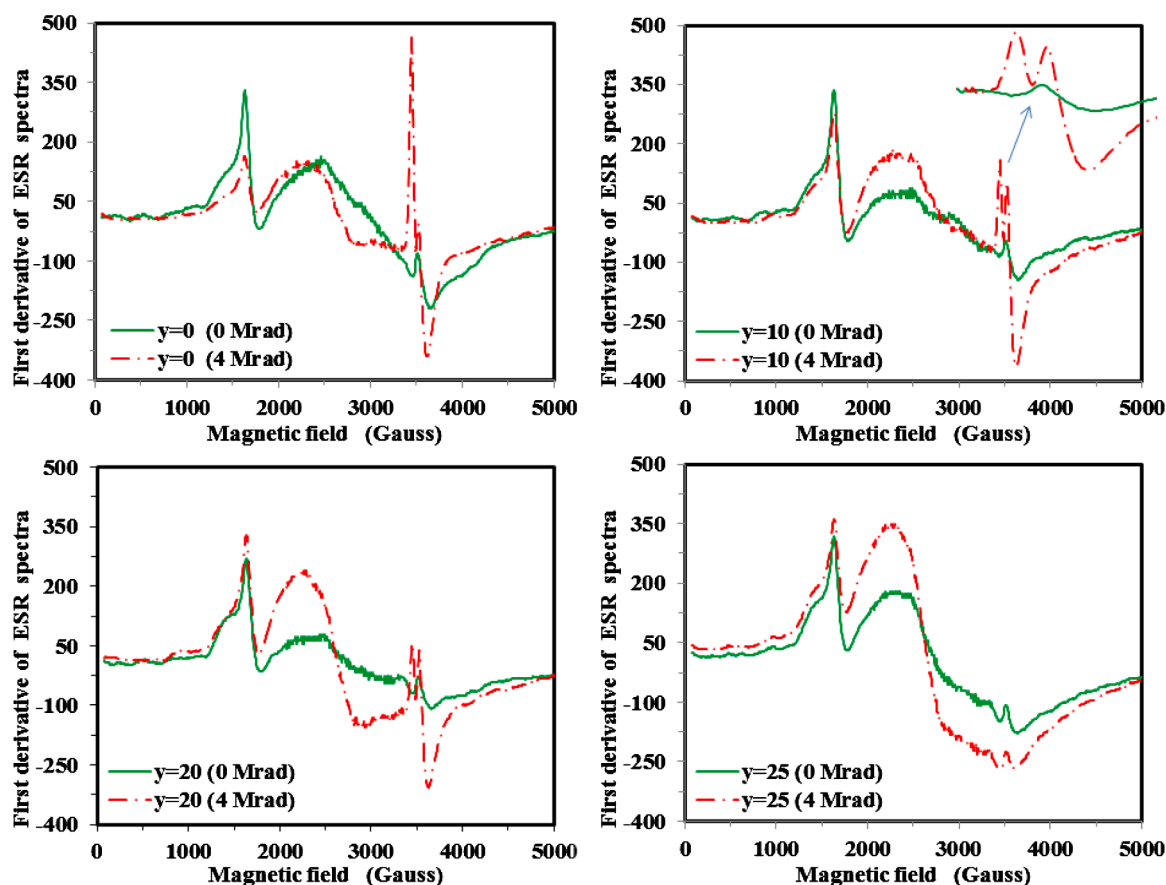


Fig. 4. ESR spectra for samples before and after irradiation (4Mrad).

after putting into consideration the transfer of charge from p electrons) [7,13,15,30]. Obviously, the intensity of  $\text{Cr}^{5+}$  ions signal decreased remarkably upon the increase of the content of lithium oxide before and after irradiation. This accords with optical measurements.  $\gamma$  irradiation results in some variations in the spectra of the studied glasses because of the induced defects generated via the released electron or positive holes during the irradiation process. The  $\text{Cr}^{5+}$  and  $\text{Cr}^{3+}$  with  $g = 2.21$  signals were noted to have increased after irradiation. In addition, the  $\text{Cr}^{5+}$  signal splitting revealed in the insert Fig. 4 accords with  $\text{Cr}^{6+}$  optical transitions ( $\nu_3$ ) demonstrated in Fig. 2.

### 3.4. FTIR spectral studies

The infrared spectroscopy was utilized for studying the alteration of structure in the samples because of the interactions between the various atoms. The IR absorption spectrum before and after irradiation (4Mrad) is shown in Fig. 5. The assumption was that an absorption band in IR spectra is possibly the result of the vibration of either atomic vibration or function group in the network. Many studies concerning glassy materials successfully applied this concept [43,44]. The same pattern is followed by all samples; the spectra reveals three major bands that are relevant to  $\text{BO}_3$  and  $\text{BO}_4$  units. The first is located between  $\sim 1200$ – $1600 \text{ cm}^{-1}$ , and it is commonly an attribute of the asymmetric stretching vibration mode of B–O on boron triangles  $\text{BO}_3$ . Meanwhile, the second is the splitting band ranging from  $\sim 800$  to  $1200 \text{ cm}^{-1}$ , and it is most possibly the result of B–O that stretches and rocks vibration of tetrahedral  $\text{BO}_4$  groups. The third band is located between  $\sim 600$  and  $800 \text{ cm}^{-1}$ , and it is usually an attribute of bending vibration of  $\text{BO}_3$  groups [45,46].

The observed shoulder at  $\sim 550 \text{ cm}^{-1}$  is assigned to Zn–O tetrahedral bending vibrations of  $\text{ZnO}_4$  units [47,48]. An occurrence of weak overlapping absorption band is noted at  $\sim 460 \text{ cm}^{-1}$  and this might have

emanated from the existence of Cr ions in hexavalent state  $\text{Cr}^{6+}$  [13]. The presence of an absorption band is noted at less than  $\sim 460 \text{ cm}^{-1}$  (marked by #), and this is possibly attributed to alkali ions that modify site vibrations [49].

Furthermore, the IR spectra of radiated samples under study have shown almost similar spectral features as ones exhibited prior to irradiation, demonstrating minor changes in the intensities of some absorption peaks. Thus, the obtained samples show more stability upon exposure to  $\gamma$  irradiation [22,23,50]. For obtaining substantial information regarding the structural groups in the samples, the spectra are deconvoluted into the minimal number of bands utilizing Gaussian line shapes. A definition of  $N_4$  is given as the ratio of the  $\text{BO}_4$  units to the total ( $\text{BO}_3 + \text{BO}_4$ ) units [51–53]. Fig. 6 shows the tendency of  $N_4$  factor to decrease upon the increase of the concentration of Li ions. This allows the assumption that increasing  $\text{Li}_2\text{O}$  ions results in changes in the structural units and the formation of NBO in the glass matrix. This can be attributed to higher field strength modifier cation ( $\text{Li} > \text{Na}$ ), where favor the creation of highly charged NBO [54]. The limited decrease noted in  $N_4$  after irradiation is possibly the result of the induced structural defects generated in the glass matrix via breaking bonds [22,23].

## 4. Conclusions

The optical absorption spectrum of alkali borate glass containing Cr ions was found to be tendency depending on the lithium oxide content which emanated in modification in the  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  optical transition. Specifically, upon the increase of the lithium content  $\text{Cr}^{6+}$ , a decrease of contribution occurs. Dq decreases upon increasing  $\text{Li}_2\text{O}$  content, while both the Racah parameters B and C values clearly follow a reverse behavior. The chromium ion environment is more ionic, and larger numbers of electrons are positioned on the d-shell. The optical band gap

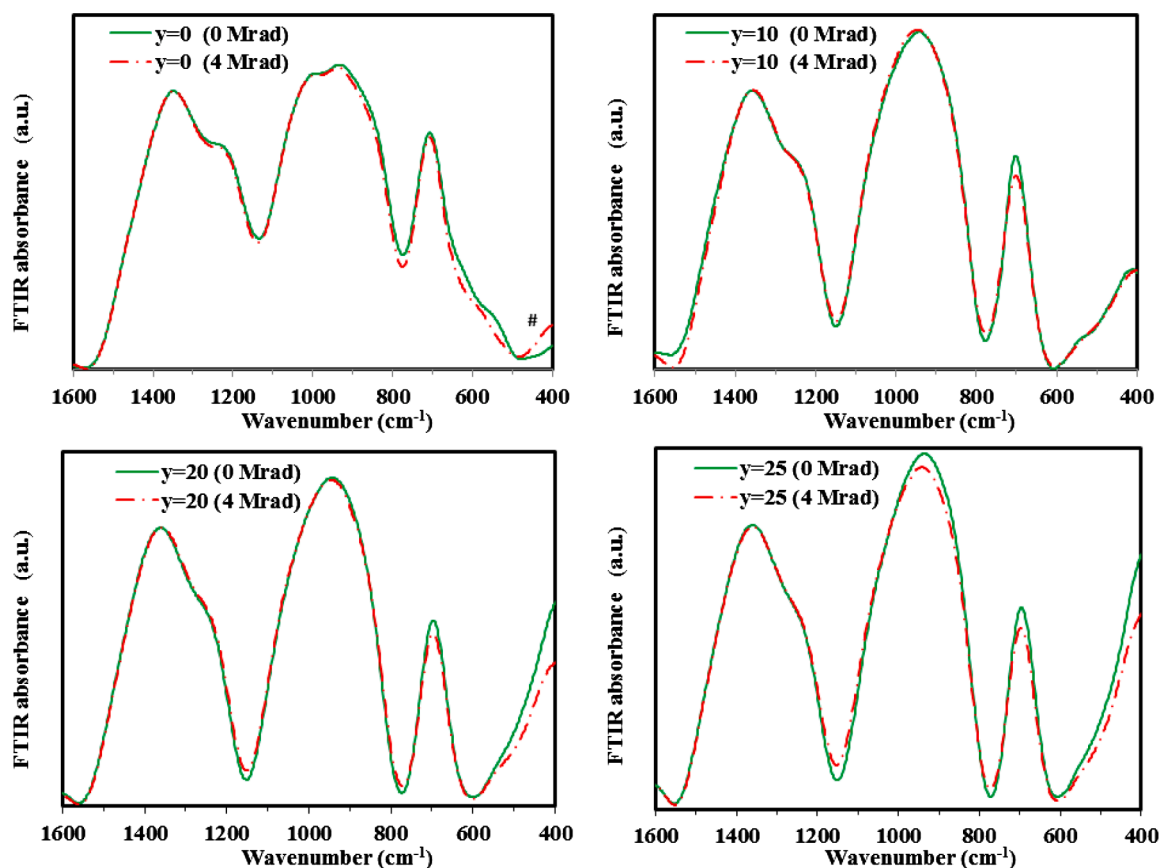


Fig. 5. FTIR absorption spectra for samples before and after irradiation (4Mrad).

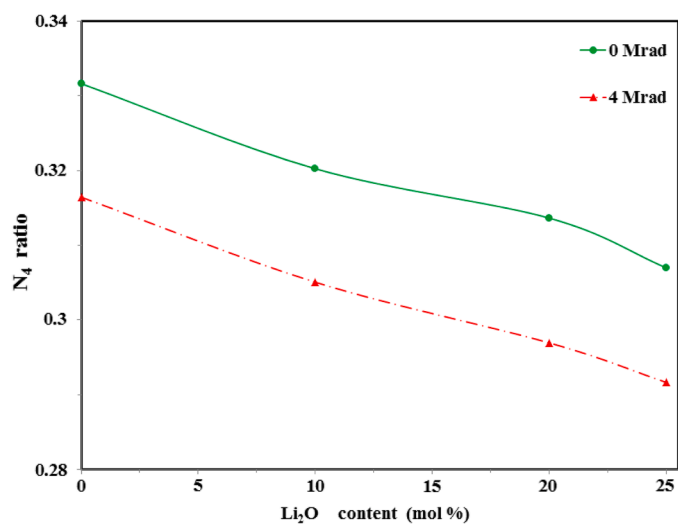


Fig. 6. represents  $N_4$  ratio for samples before and after irradiation (4Mrad).

and Urbach energies have been estimated from the ultraviolet absorption edges. ESR spectra assert the existence of hexavalent and trivalent Cr ions within host glass matrix. The FTIR absorption spectra revealed nearly no alteration of the position of most absorption bands after irradiation. So the obtained samples are more stable upon the exposure to  $\gamma$  irradiation.

#### Credit authorship contribution statement

A. I. Ismail: Samples Preparation and writing original draft

A. Samir: Samples Preparation and Results and Discussions  
 F. Ahmad: Results and Discussion and Revisions  
 L. I. Soliman: Supervision  
 A. Abdelghani: Supervision

#### Declaration of Competing Interest

No conflict of interest exists.

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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