



Ligand field and spectroscopic investigations of cobalt doped erbium–zinc borate glasses

M. Farouk¹ · F. Ahmad² · A. Samir³

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Abstract

The glasses of the composition $[x\text{CoO}-(29.5-x)\text{Na}_2\text{O}-55\text{B}_2\text{O}_3-15\text{ZnO}-0.5\text{Er}_2\text{O}_3]$ (where $x=0, 0.3, 0.5, 1$ and 3 mol%) have been prepared using melt quenching technique. The recorded UV/VIS/NIR absorption spectra have been studied and the resulting data was used for the ligand field theory analysis, from which the crystal field energy ($10Dq$), Racah parameters (B, C) and nephelauxetic ratio (β) were evaluated. The observed variations in the band gap and Urbach energy with CoO content have been discussed in relation with the glass structure. FT-IR spectra of the samples exhibit modes of vibration corresponding to the stretching of BO_3 and BO_4 unit. From IR studies, the number of non-bridging oxygens was increased, leading to loosen structure at higher CoO concentrations. The ESR spectra revealed that Co^{2+} ions are located both in distorted tetrahedral and octahedral sites.

Keywords Borate glass · Transition metal · Rare earth · Ligand field · ESR

1 Introduction

Alkali borate glasses are important materials in electro-optic, optical fibers due to its technological aspect and in nonlinear devices for frequency conversion in the UV region and piezoelectric actuator (Gaafar et al. 2013). In particular, the alkali oxide additives allow good mechanical stability and hygroscopic property of glass network (Hivrekar et al. 2018). The rich chemistry of borate glasses offered by the ability of boron to change easily its coordination with oxygen's between three and four, renders these glasses as optimistic host for TM ions (ElBatal et al. 2014). In addition, alkali oxides also modify the complex borate groups usually coordinated with either three or four oxygen atoms forming BO_3 or BO_4 structural units and by the creation of NBOs (Edukondalu et al. 2013; Kumari et al. 2012; Morsi et al. 1986). ZnO enters the host matrix of the glass in the form of both network former and modifier. Specifically, ZnO acting as a network modifier is known to significantly modify different glass

✉ A. Samir
ahmed.soliman01@feng.bu.edu.eg; ahmed.s2000@yahoo.com

¹ Physics Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo 11884, Egypt

² Department of Physics, Faculty of Science, Al-Azhar University, Girls Branch, Cairo 11754, Egypt

³ Engineering Mathematics and Physics Department, Faculty of Engineering at Shoubra, Benha University, Cairo 11629, Egypt

properties (Gaafar et al. 2013; Raghavendra Rao et al. 2011; Lakshminarayana and Buddhudu 2006). The sensitive optical response of TM ions to the glass environment has traditionally been used to map this aspect of glass structure (Morsi et al. 1986). Cobalt ions in glasses and glass ceramics are considered as handy for nonlinear optical absorbers essential for passive modulations of laser beam and for Q-switching devices (Nagarjuna et al. 2010; Rajyasree et al. 2013a). Cobalt ions can exist glasses in two stable ionic states, namely Co^{2+} and Co^{3+} . Co^{2+} ions create color centers [thick blue color in glasses and its color shade changes with the tetrahedral (T_d) to octahedral (O_h) coordination] with characteristic absorption bands in the visible and NIR spectral regimes (Lakshminarayana and Buddhudu 2006; Satyanarayana et al. 2009). Furthermore, CoO is an anti-ferromagnetic material and highly stable in ambient environment. When incorporated into a host, it improves the sintering behavior of the host and could offer wide range of applications in various industrial sectors like super capacitor, gas sensor, solar selective absorber, fuel cells and catalysis (Mimouni et al. 2015; Manickam et al. 2016; Gardavský et al. 1981; Kaczmarek 2002). The color produced due to cobalt-doped glasses depends on factors, such as the CoO concentration, experimental conditions and nature of the glass host (Gardavský et al. 1981). For example, a brilliant distinctive blue or pink color are imparted by Cobalt ions in glasses from ancient Egyptian times, and are often used as glass filters, acid–base or radiation-sensitive indicators (Abdelghany et al. 2014). The electronic configuration of Co^{2+} ion has the d^7 , which in octahedral coordination it exhibits three absorption bands associated with the spin-allowed transitions from ${}^4T_1(F) \rightarrow {}^4T_2(H)$, ${}^4T_1(4F) \rightarrow {}^4A_2(4F)$ and ${}^4T_1(4F) \rightarrow {}^4T_1(4P)$. Likewise, Co^{2+} in tetrahedral symmetry exhibits two transitions from ${}^4A_2(4F) \rightarrow {}^4T_1(4P)$ and ${}^4A_2(4F) \rightarrow {}^4T_{1g}(4F)$ (Farouk 2017). As a ligand rule, octahedral symmetry is favored over tetrahedral, but other factors, such as ionic radius, polarizability and Jahn–Teller distortion can modify the optical results. The only known ion having the $3d^7$ configuration is Co^{2+} (Abdelghany et al. 2014). A great deal regarding the electronic and vibrational properties of amorphous materials can be learned from optical absorption studies, in addition to the specific contribution from impurities such as TM ions (Farouk 2017; Bale and Rahman 2009). Likewise, rare-earth ions in oxide glasses are also stable hosts for obtaining efficient luminescence (Zhao et al. 2008). The Er^{3+} doped optical materials find applications in visible and near infrared lasers, fiber amplifiers, temperature sensor and color display (Vijayalakshmi et al. 2018). Therefore, the combination of TM and rare-earth ions within the same host is expected to allow for highly featured absorption spectra spanning the entire visible and near-infrared spectral regimes. For instance, such TM-rare-earth hybrid hosts can efficiently harvest the visible light and could find application in photovoltaic energy conversion. Electron spin resonance (ESR) can be applied to study about TM ions doped in glass systems. This technique gives the characterization of local structure of a paramagnetic center and also structural changes within glasses (Santhan Kumar et al. 2013). The aim of this work is to synthesize $x\text{CoO}-(29.5-x)\text{Na}_2\text{O}-55\text{B}_2\text{O}_3-15\text{ZnO}-0.5\text{Er}_2\text{O}_3$ glass with different CoO concentrations, and to characterize by a variety of spectroscopic techniques, the optical absorption, IR and ESR of the cobalt ions environment in the glass network. The observed absorption bands were interpreted well in terms of ligand field theory.

2 Experimental

The glasses of composition $x\text{CoO}-(29.5-x)\text{Na}_2\text{O}-55\text{B}_2\text{O}_3-15\text{ZnO}-0.5\text{Er}_2\text{O}_3$ ($x=0, 0.3, 0.5, 1$ and 3 mol%) were prepared by melting and quenching technique. The weights of chemicals were mixed homogeneously and taken in a porcelain crucible and put in furnace

at 1160 °C for 1 h. The glass melts were pouring and pressing between two brass moulds. The disc shaped glass samples with thickness of about 1 mm were used for characterization. The optical absorption spectra of glasses were measured in the wavelength range 200–2200 nm by using a double beam UV/VIS/NIR spectrophotometer (type JASCO Crop., V-770, Japan). FT-IR absorption spectra of all samples were measure by using (FT-IR Nicolet 6700) spectrometer in the range of 400–4000 cm^{-1} using KBr pellet technique. The Electron spin resonance ESR spectra are recorded on ESR spectrometer (EMXBruker), operating in X-band frequency ($\nu=9.154$ GHz) at room temperature. The magnetic field was scanned from 75 to 6000 Gauss. The spectra have been normalized by maintaining a unit mass (g) through dividing the ESR signal by its mass.

3 Results and discussion

3.1 Optical absorption

Figure 1 represents the cobalt doped alkali zinc borate glass, which has a strong absorption band start from the UV to the visible region, and band in the NIR. The absorption spectra of Er/Co ions co-doped glasses show a number of bands. The assignment of the observed bands is made on the basis of the reported energy levels of Er^{3+} ions doped in different glass hosts (Kaky et al. 2017; Haouari et al. 2017; Kesavulu et al. 2016). With CoO additives, the absorption intensity enhances and exhibits absorption band. In the free cobalt sample several bands are observed in Fig. 2. The absorption spectra of NIR region can be seen in more detail. These bands are fingerprint for Er^{3+} ion $4f-4f$ transitions from ground state to various excited levels. The bands are related to Er^{3+} ions resulting due to the different transitions are from ${}^4I_{15/2} \rightarrow {}^4G_{9/2}$, ${}^4G_{11/2}$, ${}^2H_{9/2}$, ${}^4F_{3/2}$, ${}^4F_{5/2}$, ${}^4F_{7/2}$, ${}^2H_{11/2}$, ${}^4S_{3/2}$, ${}^4F_{9/2}$, ${}^4I_{9/2}$, ${}^4I_{11/2}$, ${}^4I_{13/2}$ (Jamalaiah et al. 2012; Farouk et al. 2013). When CoO is added to the glass network additional bands are observed at 519, 586, 639 and 1492 nm. Thus, from these optical spectra the overall bands are observed for Er^{3+} and Co^{2+} co-doped glass samples as shown in Fig. 1.

The strong UV/VIS absorption bands at 519, 586 nm are attributed to the transitions ${}^4T_{1g}({}^4F) \rightarrow {}^2T_{1g}(H)$ of octahedrally coordinated (O_h) Co^{2+} and ${}^4A_2({}^4F) \rightarrow {}^4T_1({}^4p)$ of tetrahedrally coordinated (T_d) Co^{2+} , respectively. The broad absorption band at 1435 nm is

Fig. 1 Represents the UV/VIS/NIR of optical absorption spectra of cobalt doped alkali zinc borate glass

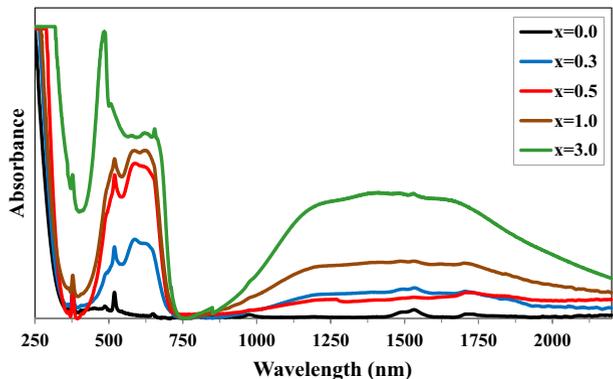
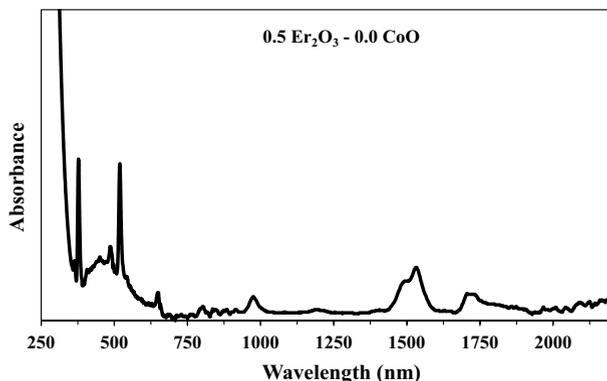


Fig. 2 Optical absorption spectra of the investigated glass doped with Er^{3+} (free cobalt sample) all transitions are from the ground state $^4I_{15/2}$



assigned to the allowed transition $^4A_2(^4F) \rightarrow ^4T_{1g}(^4F)$ of tetrahedrally coordinated Co^{2+} (Ahmad et al. 2014; Abdelghany et al. 2018).

Moreover, optical spectra exhibited one octahedral band due to $^5T_{2g} \rightarrow ^5E_g$ of Co^{3+} ions at about 639 nm (Farouk 2017; Abd El-Fattah et al. 2017; Okasha et al. 2017). As the CoO concentration is increased, the intensity of tetrahedral bands grows as well as octahedral band. The ligand field theory was applied to analyze the observed octahedral (d^3 electronic configuration) and tetrahedral of Co^{2+} (d^7) field transitions in glassy system (Farouk 2017; Ahmad et al. 2014; Rajyasree et al. 2013b).

From the estimated positions of the experimental allowed transitions (as shown in Fig. 1), the crystal field parameters such as $10Dq$ crystal field parameter and the Racah parameter B , C ($C \approx 4.5 B$) can be calculate from the relations (Farouk 2017; Ahmad et al. 2014; Beaury et al. 2004):

$$B = \frac{1}{510} \left[7(\nu_2 + \nu_3) \pm \left\{ 49(\nu_2 + \nu_3)^2 + 680(\nu_2 - \nu_3)^2 \right\}^{1/2} \right]$$

$$10Dq = \frac{1}{3}(\nu_2 + \nu_3) - 5B$$

The values of the nephelauxetic ratio (β) measure the covalency for Co^{2+} ion in glasses. For all samples, the obtained values of Dq , B , C and β are listed in Table 1. It is clear that, the crystal field $10Dq$ and the Racah parameters decreases up to 0.5 mol% then increases with CoO content. This can be attributed to the increased inter-electronic repulsion between d -orbital electrons, leading to the creating of partially covalent bonds in glassy system (Ahmad et al. 2014; Rajyasree et al. 2013b). The overlapping of transitions of Er^{3+} and Co^{2+} ions is likely due to transition metal and rare earth mixture as seen in Fig. 1.

Figure 3 shows the deconvolution of the overlapping spectra of different contributions to the definition of the Er^{3+} and Co^{2+} optical absorption spectrum in the visible region. From the observed edge, we have evaluated the optical band gap (E_{opt}) of the glasses by drawing between $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for indirect transitions according to the following standard relation (Farouk et al. 2018):

$$\alpha h\nu = B(h\nu - E_g)^n$$

where B is a constant reflecting the extent of band tailing and $h\nu$ is the incident photon energy. The respective values of E_{opt} are obtained by extrapolating of the linear part of the curve to $h\nu$ axis where $(\alpha h\nu)^{1/2} = 0$ as shown in Fig. 4. The determined values of E_{opt} of

Table 1 The absorption transitions, optical parameters and ligand field parameters of cobalt ions doped glasses

x (mol%)	Band positions (nm)		Optical parameters				Ligand field parameters			
	CO ²⁺		CO ³⁺				Dq (cm ⁻¹)	B (cm ⁻¹)	C (cm ⁻¹)	β
	$^4T_{1g}(F) \rightarrow ^2T_{1g}(H)$	$^4A_2(^4F) \rightarrow ^4T_1(^4p)$	$^4A_2(^4F) \rightarrow ^4T_{1g}(^4F)$	$^5T_{2g} \rightarrow ^5E_g$	E _{opt} (eV)	ΔE (eV)				
0	–	–	–	–	–	–	–	–	–	–
0.3	519	586	1492	639	3.38	0.33	482	620	2789	0.638
0.5	511	590	1516	649	3.39	0.31	478	613	2760	0.632
1	496	587	1505	648	3.46	0.19	481	617	2777	0.635
3	477	502	1408	673	3.29	0.43	552	697	3138	0.781

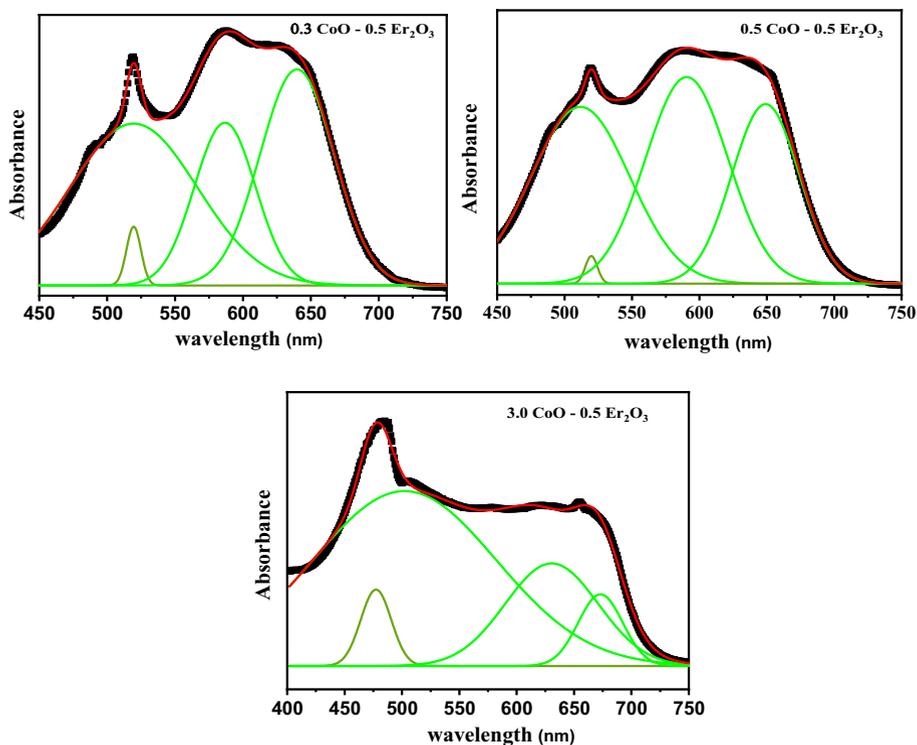


Fig. 3 Deconvolution of the overlapping spectra of different contributions to the definition of the Er^{3+} and Co^{2+} of glass samples

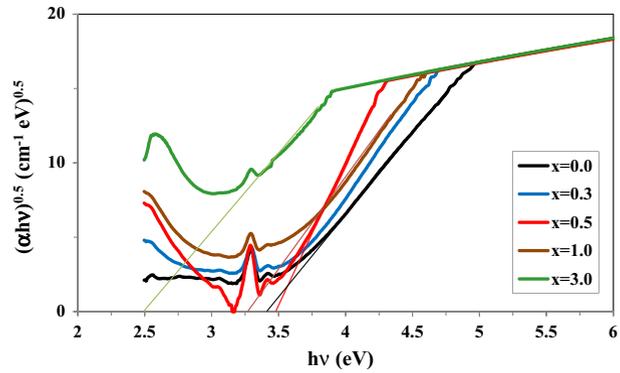
the glass samples are summarized in Table 1. With increasing the CoO concentration up to 0.5 mol%, a considerable increase in the optical band gap of glass samples is observed after that it decreases with CoO content.

Urbach energy provides the width of states localized within the optical band gap. At the absorption edge, the broadening of excitation level is dominated by random internal electric fields due to presence of defects (Farouk et al. 2018). The main characteristic of the absorption edge of non-crystalline materials is the exponential relation of the absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$, which is given by the following Urbach rule (Samir et al. 2019).

$$\alpha = c \exp(h\nu/\Delta E)$$

where C is a constant and ΔE is the Urbach energy determined from the reciprocals of slopes of the linear part of $\ln(\alpha)$ versus photon energy $h\nu$ (not shown). The values of Urbach energy for all samples are given in Table 1. It has been reported that ΔE lies between 0.045 and 0.66 eV for amorphous semiconductors (Sumalatha et al. 2011), in agreement with the values here reported. Furthermore, the Urbach energy is decreased with increasing CoO content up to 0.5 mol% then, it increased with higher content of CoO. The increase of Urbach energy and hence, the decrease of optical band gap is likely due to octahedrally coordinated Co^{2+} ions which act as modifier and induce NBOs in the glass network as inferred later from FTIR results(Rajyasree et al. 2013b).

Fig. 4 Plot of $(\alpha h\nu)^{1/2}$ v/s $h\nu$ for indirect band gap energy(E_{opt}) measurements



3.2 FTIR spectra

Infrared spectroscopy is often used to gain important information regarding the structural unit's arrangement within the studied glass. Within the glass network, it is generally assumed that the vibrations of structural units are independent on the vibration of the other neighboring units (Pascuta et al. 2009). The observed infrared spectra of these glasses arise largely from the modified borate networks and are mainly active in the spectral range $400\text{--}1600\text{ cm}^{-1}$; therefore the spectra are shown in this range for better clarity. The infrared spectra of the samples, recorded at room temperature, are shown in Fig. 5, while the position of various vibrational bands and their assignments are tabulated in Table 2.

The deconvolution of obtained infrared spectra of all studied glass samples was made by using origin software (version 2018) to identify all bands (Rammah et al. 2019). For better identification of peaks, the given data have been deconvoluted and a typical deconvoluted spectra for $x=0.0$ mol% glass sample is shown in Fig. 6. Following the literature, vibrational modes of the borate network are known to be mainly active in three infrared spectral regions. The first groups of bands at $1200\text{--}1600\text{ cm}^{-1}$ are due to the asymmetric stretching vibration of the B–O band of trigonal BO_3 units (Ahmad et al. 2014; Subhashini and Shashikala 2016; Thakur et al. 2015). The second group between 800 and 1200 cm^{-1} is usually assigned as B–O bond stretching of the tetrahedral BO_4 units. The third group is usually observed in the region $600\text{--}800\text{ cm}^{-1}$ and is due to the bending vibrations of B–O–B in BO_3 units (Rajyasree et al. 2013a; Naga Raju

Fig. 5 FT-IR spectra of the glassy system doped with different concentrations of CoO

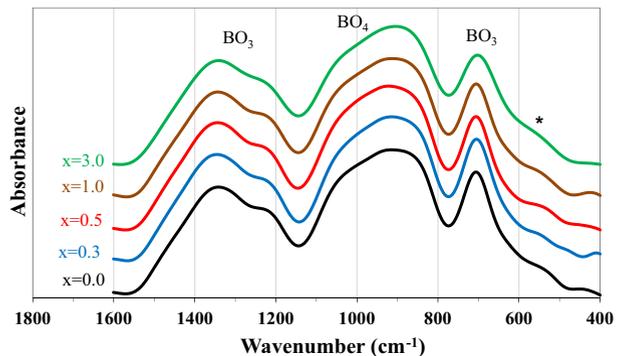
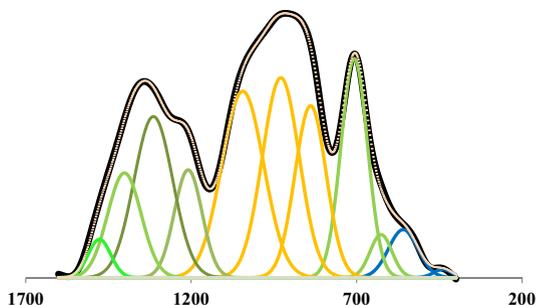


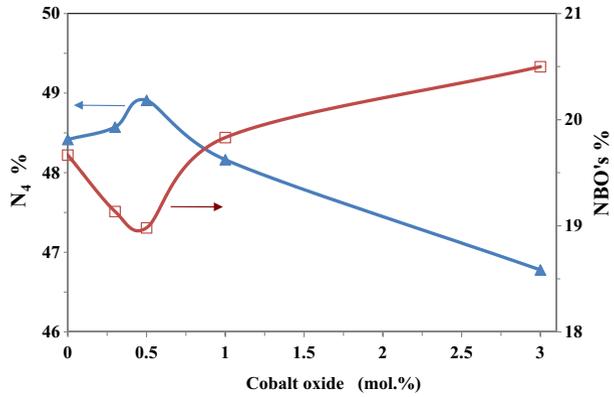
Table 2 Assignment of the FTIR bands of the glass samples

Band position (cm ⁻¹)	Assignment
~ 450	Specific vibrations of Na–O bonds
~ 560	Presence of Zn–O tetrahedral bending vibrations of ZnO ₄ units
600–800	Bending vibrations of B–O–B in BO ₃ units
~ 840	Stretching vibrations of the NBOs of BO ₄
800–1200	B–O bond stretching of the tetrahedral BO ₄ units
~ 1220	Stretching vibrations of the NBOs of BO ₃
1200–1600	Asymmetric stretching vibration of the B–O band of trigonal BO ₃ units

Fig. 6 Deconvoluted infrared bands for x = 0.0 mol% as an example

et al. 2006; Stoch and Sroda 1999; Waclawska 1995; Kamitsos et al. 1990, 1993; Krogh-Moe 1969). Additional band ~ 450 cm⁻¹ is developed which may be due to the specific Na–O cation vibrations (Abdelghany et al. 2014; Abd El-Fattah et al. 2017; Subhashini and Shashikala 2016). In the present glassy system ZnO tetrahedron [ZnO_{4/2}] vibrates at ~ 560 cm⁻¹ indicates the presence of Zn–O tetrahedral bending vibrations of ZnO₄ units (Ahmad et al. 2014; Naga Raju et al. 2006; Abdel-Baki and El-Diasty 2011). This assures that ZnO preferentially acts as a network former. By introduction of cobalt oxide content, the ZnO absorption band becomes more broad which due to overlapping with specific vibrations of Co³⁺ ions (marked by *) (Abd El-Fattah et al. 2017; Rao et al. 2002). The absorption bands at ~ 840 and ~ 1220 cm⁻¹ are attributed to the stretching vibrations of the NBOs of BO₄ and BO₃ groups, respectively (Gaafar et al. 2013; Abdel-Baki and El-Diasty 2011; Błaszczak et al. 2004). The tetrahedrally coordinated boron atoms fraction N₄ [B₄/(B₃ + B₄), where, B₃ and B₄ represent the area of peaks corresponding to [BO₃] and [BO₄] groups], can be calculate after performing a deconvolution process (Hivrekar et al. 2018; Rammah et al. 2019). Deconvolution enables the calculation of the fraction of the four coordinated boron atoms, N₄, from the infrared spectra. The relative area of the deconvoluted bands indicates the variation in N₄ in the structure. From Fig. 7 it is clear that, N₄ increases with 0.5 mol% doping of CoO. It may be due to formation of tetrahedral Co²⁺ ions (CoO₄ units) which act as formers in the glass matrix. The decrease in N₄ with further addition of CoO is due to the increasing presence of cobalt ions in octahedral positions (CoO₆ units) which destroy BO₄ units. Therefore, NBOs will be induced along with a reduced rigidity of the glass network, as shown in Fig. 7 (Gaafar et al. 2013; Rajyasree et al. 2013b).

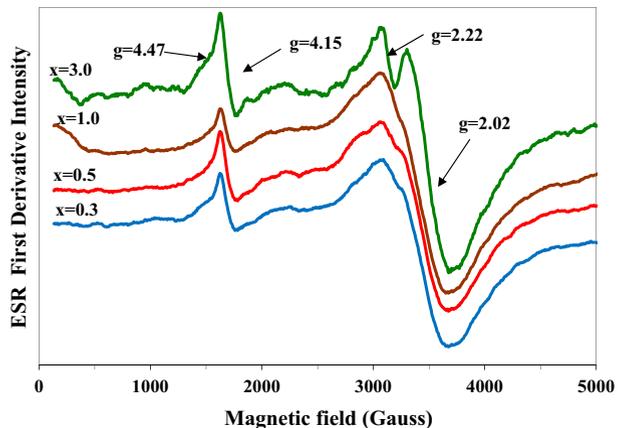
Fig. 7 Variation of N_4 and NBO's ratio with cobalt oxide content



3.3 ESR spectra

ESR spectroscopy is the important tools to confirm the structure of some ligand type around the Co ions. It is one of the useful methods for studying materials with unpaired electrons and confirm on the oxidation states of Co species present in the prepared samples. Co^{2+} ions can form both octahedral and tetrahedral coordination spheres. Figure 8 shows the ESR spectra of the prepared glassy system. These ESR signals refer to presence of paramagnetic Co^{2+} ions (Arshadi et al. 2011). The spectra have been normalized by maintaining a fixed mass for samples through dividing the intensity by the corresponding factor. The spectra exhibited a resonance lines at 1542 and 1659 G with $g=4.47$ and 4.15, respectively. These are attributed to Co^{2+} ions located in octahedral symmetry crystal fields (Abd El-Fattah et al. 2017; Rajyasree et al. 2013b; Jiro et al. 1989; Sreedhar et al. 1996). In addition to a resonance lines are observed centered at ~ 3108 and 3418 G with $g=2.22$ and 2.02, respectively which is assigned to Co^{2+} ions in a tetrahedral crystal field (Abd El-Fattah et al. 2017; Jiro et al. 1989). The asymmetry of the resonance lines increases with CoO additives. It could be due the superposition of two signals; one is due to isolated Co^{2+} ion and the second ESR signal results from interacting Co^{2+} ions coupled as clusters by

Fig. 8 ESR spectra of cobalt doped glasses



exchange coupling (Pal et al. 2013). Besides, it's due to a random distribution of distortions (Sreedhar et al. 1996). It is clear that CoO addition enhances the intensity of Co^{2+} tetrahedral as well as octahedral resonance lines as obviously in optical spectra.

4 Conclusion

In this work, the effect of CoO content on the physical, structure and optical properties of cobalt doped erbium–zinc borate glasses is studied. It is observed that the E_{opt} increases with increasing of CoO content up to 0.5 mol%, after that it decreases with increasing CoO content, while the Urbach energy shows opposite trend. The values of $10Dq$, B , C and β for all samples are estimated and studied. FTIR spectra of the present glass system contain different band characteristics for BO_3 , BO_4 and $\text{ZnO}_{4/2}$ structural units. The ratio N_4 were estimated and studied. It is clear that CoO addition enhances the intensity of Co^{2+} tetrahedral as well as octahedral resonance lines as observed in optical spectra.

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