Optical transitions from hexavalent chromium in lithium-borate glasses

Dhia-Aldin Slibi1 · Moukhtar A. Hassan1 · Zakaria M. Abd El-Fattah1 · M. Atallah2 · M. A. El-Sherbiny1 · M. Farouk1

Received: 7 March 2021 / Accepted: 24 July 2021 / Published online: 14 August 2021
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

Abstract
The melt-quenching technique was used to prepare a series of chromium-doped borate glasses with the composition $x\text{Cr}_2\text{O}_3 - (70-x) \text{B}_2\text{O}_3 - 30 \text{Li}_2\text{O}$ ($x=0, 0.1, 0.2, 0.3$ and $0.5$ mol %). The low-doping level here employed allowed to unambiguously identify well-defined near-edge $\text{Cr}^{6+}$ optical transitions, and to precisely determine the optical band gap of the borate glass host. Additional $\text{Cr}^{3+}$ transitions were observed in the visible regime, rendering a strong modulation of the glass color, from colorless to dark greenish, with Cr content. Both $\text{Cr}^{6+}$ (after the charge transfer transformation into $\text{Cr}^{5+}$) and $\text{Cr}^{3+}$ oxidation states and their variations with Cr doping were identified from electron spin resonance spectroscopy. All samples exhibit similar vibrational spectra dominated by $\text{BO}_3$ and $\text{BO}_4$ structural units, with the development of weak $\text{Cr}^{6+}$ vibration with Cr doping. The present study provides structurally similar but optically active and tunable glass hosts suitable for various optical applications.

Keywords Chromium hexavalent/Trivalent · Borate glasses · Colored glasses · UV–Visible optical devices · ESR

1 Introduction
Colored glasses acquired a lot of interest in commercial business as they are favored in home decoration and many other technological applications. Optical transitions between energy split $d$ and $f$ levels in transition metals (TM) and rare earth ions, respectively, are the main origin for color effects (Hassan et al. 2018, 2019, 2012; Ahmad and Nabhan 2019; Wen and Tanner 2015; He 2016; Daishan et al. 2019; Abd El-Fattah et al. 2017; Samir et al. 2019; Wen et al. 2016). For precise and controlled tunability of glasses color, for example, it is appealing to search for suitable glass hosts capable of accommodating...
varies concentrations of TM ions. For this purpose, alkali borate glasses are convenient host given its low cost, transparency, and chemical/thermal stability (Hassan et al. 2012; Wen et al. 2016; Venkateswara Rao and Veeraiah 2002; Terczyńska-Madej et al. 2011; Pisarski et al. 2009). Most importantly, alkali-borate glasses act as efficient TM hosts, since they offer two distinct structural units ($BO_3$ or $BO_4$), in addition to their possible conversion when doped with alkali oxides (Wen et al. 2016; Venkateswara Rao and Veeraiah 2002; Terczyńska-Madej et al. 2011; Pisarski et al. 2009). Chromium is a TM ion that offers different oxidation states (such as $Cr^{3+}$, being the most stable, $Cr^{4+}$, $Cr^{5+}$ and $Cr^{6+}$) playing different rules (former or modifier) in glassy matrix depending on its valence state (Hassan et al. 2019). Low level doping of chromium ions in glasses causes color variations, the degree of which depends on its concentration. Moreover, $Cr^{3+}$ ions have significant sensitivity to possible structural changes that affect the optical and magnetic properties (Farouk et al. 2021). The random structure of glasses renders different environment for each $Cr^{3+}$ ion as a consequence of differences in bonding to nearest-neighbor ions. This results in site-to-site variations in the energy level structure and, consequently, to radiative and non-radiative transition probabilities of $Cr^{3+}$ ions in glasses (Chattjee and Forster 1964). Therefore, the optical absorption spectra will be a convolution of cooperating individual crystal-field sites.

In this study, the optical absorption and electron spin resonance (ESR) spectroscopies were used to probe the optically active $Cr^{6+}$ and $Cr^{3+}$ optical transitions for different Cr content. The borate glass as a host and the minimal amounts of Cr doping levels are chosen aiming to reduce the strong absorption for Cr ions near the absorptions edge. For such diluted Cr-doped system it was then possible to resolve the discrepancies reported for the correct estimation of the band edge in the presence of $Cr^{6+}$ transitions.

2 Experimental

The selected glassy compositions $xCr_2O_3-(70-x) B_2O_3–30 Li_2O–(x = 0, 0.1, 0.2, 0.3$ and 0.5 mol %) were prepared by conventional melt quenching technique. Appropriate quantities of chemicals [Cr$_2$O$_3$, B$_2$O$_3$, and LiO$_2$] were weighted according to their molar rations, mixed, and ground finely in an agate mortar to achieve high homogeneity of reactants. The batches were placed in porcelain crucibles and eventually melted in an electrical furnace at 950 °C for 1 h. The melts were taken out after 30 min of heating process and packed into furnace for additional 30 min. In order to fabricate bubbles-free glass pellets, the melts were quenched in air between two well-polished copper plates at room temperature. The geometry of the as quenched samples is often in the form of irregular flakes of lateral area ~ 4 cm$^2$ and thickness variations between 1.2 mm and 1.0 mm. The chromium-free sample was found to be colorless, while other samples became greener with increasing Cr content. The structural and optical properties of the samples were explored by utilizing a set of complementary techniques. X-ray diffraction (XRD) data were collected in the range 10–90°, in steps of 0.02°, using SHIMADZU-6000-type diffractometer equipped with CuKα X-ray source ($\lambda = 1.541$ Å). Fourier transform infrared absorption spectra were obtained at room temperature using FTIR (Perkin Elmer) spectrophotometer in the range 2200–400 cm$^{-1}$. The samples were ground, and the resulting powders were thoroughly mixed with high purity KBr. Optical absorption spectra of all glasses were carried out using UV–VIS spectrophotometer (JenWay-6405 UV–VIS Spectrophotometer) in the range 200–1000 nm. ESR spectra were recorded using an EMX-Bruker operating in
X-band frequency, and having 100 kHz field modulation. The power of the used microwave was 10 mW, and a fixed amount of glass powder from each sample was inserted in a quartz tube, while the magnetic field was scanned in the range 75–5000 G.

3 Results and discussion

3.1 X-Ray Diffraction

XRD patterns of Cr-free and two selected Cr-doped (x = 0, x = 0.2, and x = 0.5 mol. %) samples are presented in Fig. 1. The spectra contain broad humps originating from atomic scale short-range order characteristic for borate glasses (Dahshan et al. 2019; Pisarski et al. 2009). The absence of well-defined diffraction signals in the wide angular range (10–90°) ensures the amorphous nature of the prepared samples.

3.2 Optical Absorption Results

The optical absorption spectra for all glass systems are given in Fig. 2. The spectrum of Cr-free (i.e., x = 0) sample is featureless, except for a well-defined absorption edge at ~ 3.57 eV (black arrow) defining the band gap energy of the host. A first insight into the optical absorption spectra of Cr-doped samples reveals remarkable changes of the energetic position of the absorption edge, and the development of distinct optical transitions characteristic for Cr ions, as indicated by red and blue arrows.

For an accurate determination of the absorption edge and energetic position of Cr bands comprising such multi-feature spectra, a detailed deconvolution process is applied for all samples. Example of such deconvolution routine is shown in Fig. 3a exclusively for the x = 0.3 mol % sample. The spectrum is fitted by employing five Gaussian peaks, two red (are Cr⁶⁺ bands) and three blue (are Cr³⁺ bands), and a Fermi-like edge function (dashed-black) for the absorption band gap. The sum of the Gaussian peaks and edge function

Fig. 1 XRD patterns for three selected samples

![Fig. 1 XRD patterns for three selected samples](image-url)
yields the black curve, which nicely coincide with the experimental data. To estimate the optical band gap, we apply the Tauc’s plots on the deconvoluted absorption edges as shown in Fig. 3b, and the obtained values are given in Table 1. The band gap energy exhibits a slight reduction (~0.2 eV) with increasing Cr$_2$O$_3$ content, due to the increase of the electronic contribution from high coordination number of Cr oxidation states (Othman et al. 2021).

Notice that, for the maximum doping level here used (i.e., sample with $x = 0.5$), the apparent absorption edge could mislead the estimation of the band gap to be ~2.6 eV. Such a noticeably large change in the band edge (~1 eV) for such a tinny Cr-doping ($x = 0.5$) is unpredictable, although earlier borate-related literature reported underestimated energy gaps within the range 2–2.5 eV (Ahmad 2014; Kesavulu et al. 2010; Hassan 2013; Naga Raju et al. 2006; ElBatal et al. 2009; Batal et al. 2020; Sallam et al. 2020). In fact, such large underestimation of band edge position and gap size is also found for other glassy systems (Lakshmana Rao et al. 2013; Vicente et al. 2014; Vijay et al. 2015; Narendrudu et al. 2017; Sambasiva Rao et al. 2015) and TM-doped semiconductor nano materials (Habib et al. 2019; Dubey and Singh 2017; Akshay et al. 2019; Dattu Mote et al. 2012). In order to shed the light on the fine near-edge details, lower Cr-doping levels ($x < 0.5$) are used. The spectra of these slightly doped systems exhibit distinguishable near-edge absorption peaks, which lie at the origin of such misleading edge assignment. In fact, these absorption features (red arrows) are brought by Cr$^{6+}$ characteristic optical transitions commonly found at ~338 and ~370 nm, and are assigned to $^4A_{2g} \rightarrow ^4T_{1g}$ and to $^4A_{2g} \rightarrow ^2A_{1g}$ transition, respectively (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Wen and Tanner 2015; Terczynska-Madej et al. 2010; Padlyak et al. 2012; Morshidy et al. 2021; Ravikumar et al. 2005; Vijay Singh et al. 2014). Actually, Cr$^{6+}$ is optically inactive since it has 3d$^0$ configuration, but the charge

---

**Fig. 2** Optical absorption spectra for all glassy samples. The black, red, and blue arrows define the position of the absorption edge, Cr$^{6+}$, and Cr$^{3+}$ transitions, respectively. The thick white-green arrow and samples photos highlight the fine changes in the glass color with Cr-doping.
transfer taking place between O and Cr ions leads to the optically active Cr$_{5+}$ (3d$^1$ 2p$^5$) state (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Cz. Koepke, K. Wiśniewski, M. Grinberg 2002; Cz. Koepke, K. Wiśniewski, M. Grinberg, F. Rozpłoch 2002; Little Flower et al. 2007; Murali Krishna et al. 2007). The intensity of Cr$_{6+}$ peaks clearly gains more intensity with Cr-doping, until a saturation in the UV region is achieved for the $x=0.5$ sample. These findings allow concluding that the apparent huge shift of optical band edge results from the dominant Cr$_{6+}$ spectral features in this regime. Additionally, both the absorption edge and Cr$_{6+}$ peaks experience a slight red shift (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019).

**Table 1** Band gap energy and Ligand field parameters (C/B & Dq/B ratios and neplequestic parameter, $h$)

| Cr$_2$O$_3$ content (mol. %) | Band gap energy (eV) | Ligand field parameters |
|-------------------------------|----------------------|-------------------------|
|                              | $E_g$                | C/B | Dq/B | $h$  |
| 0.0                           | 3.57                | –   | –    | –    |
| 0.1                           | 3.56                | 3.77 | 2.13 | 0.804|
| 0.2                           | 3.52                | 3.80 | 2.24 | 0.962|
| 0.3                           | 3.49                | 3.83 | 2.29 | 1.046|
| 0.5                           | 3.37                | 3.79 | 2.38 | 1.177|
In the visible regime, \( \text{Cr}^{3+} \) ions feature two additional optical transitions (blue arrows) which are responsible for the glass color (Taktak et al. 2015). These bands located at \(~421 \text{ nm and } 619 \text{ nm}\) (as shown in Fig. 2) define the yellow and greenish colors, respectively. The bands originate from \( \text{Cr}^{3+} \) ions \( d-d \) transitions in octahedral environment, and are assigned to \( ^4A_{2g} \rightarrow ^4T_{1g} \) and \( ^4A_{2g} \rightarrow ^4T_{2g} \) transitions, respectively (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Terczynska-Madej et al. 2010; Padylyak et al. 2012; Morshidy et al. 2021; Ravikumar et al. 2005; Vijay Singh et al. 2014; Cz. Koepke, K. Wiśniewski, M. Grinberg 2002; Cz. Koepke, K. Wiśniewski, M. Grinberg, F. Rozploch 2002; Little Flower et al. 2007; Murali Krishna et al. 2007; Taktak et al. 2015; Lakshmana Rao et al. 1989; Durga and Veeraiah 2002; Vijay Singh and Chakrardhar 2009; Giridhar et al. 2011). These peaks systematically gain intensity and undergo a slight red shift with increasing \( \text{Cr}_2\text{O}_3 \) content, thereby changing the glass color from colorless to dark greenish as shown at the inset of Fig. 2.

The crystal field parameters, such as crystal field strength (\( 10Dq \)) and Racah parameters (\( B & C \)) can be deduced from the following equations: (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Terczynska-Madej et al. 2010; Padylyak et al. 2012; Morshidy et al. 2021; Ravikumar et al. 2005; Vijay Singh et al. 2014);

\[
10Dq = v_1 \tag{1}
\]

\[
B = \frac{(2v_1 - v_2)(v_2 - v_1)}{(27v_1 - 15v_2)} \tag{2}
\]

\[
C = \frac{v_3 - 4B - v_1}{3} \tag{3}
\]

where \( v_1, v_2 \) and \( v_3 \) refer, respectively, to the bands positioned at 619 nm (\( \text{Cr}^{3+} \)), 421 nm (\( \text{Cr}^{3+} \)) and the average sum of 337 and 369 bands (\( \text{Cr}^{6+} \)) all taken in cm\(^{-1}\) energy units. Figure 3c and d presents these field parameters as a function of \( \text{Cr}_2\text{O}_3 \) content. It is noticed that the value of \( 10Dq \) (\( B \) and \( C \)) increases (decreases) with introducing more \( \text{Cr} \) ions, indicating weaker \( d \) shell inter-electronic repulsion.

The ratio between Racah parameters (\( C/B \)) was found to be \(~3.8\) as listed in Table 1. Likewise, the ratio \( Dq/B \) is found to increase from 2.13 to 2.38 indicating a crossover from the weak to moderate crystal field with \( \text{Cr}_2\text{O}_3 \) content (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Kesavulu et al. 2010). The estimated bond formation represented as the nephelauxetic parameter (\( h \)) is given as (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Kesavulu et al. 2010; Vicente et al. 2014):

\[
h = \frac{[B_{\text{free}} - B]/B_{\text{free}}}{K_{\text{Cr}^{3+}}} \tag{4}
\]

where \( B_{\text{free}} \) defines the Racah parameter for gaseous \( \text{Cr}^{3+} \) and \( K_{\text{Cr}^{3+}} \) is the central \( \text{Cr}^{3+} \) ion, which take the values \( B_{\text{free}} = 918 \text{ cm}^{-1} \) and \( K_{\text{Cr}^{3+}} = 0.21 \) (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Vicente et al. 2014; Ravikumar et al. 2005). Therefore, for all glass samples, \( B \) is lower than \( B_{\text{free}} \), as given in Table 1. The estimated \( h \) parameter increases with \( \text{Cr}_2\text{O}_3 \) content, indicating more covalent environment for \( \text{Cr}^{3+} \) ions and increased \( d \)-electrons localization (Hassan et al. 2018; Vicente et al. 2014; Ravikumar et al. 2005).
3.3 FTIR Results

Figure 4 presents the FTIR spectra of all glass samples, while the corresponding peak assignments and energetic positions for the various fundamental vibrational units of borate and chromium networks are listed in Table 2. To obtain precise information about structural changes within the glass a detailed deconvolution process, using a number of Gaussian bands, is required. The structure of borate glasses consists of a random network of planar triangles $BO_3$ with a certain fraction of six-member rings (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Vicente et al. 2014; Cz. Koepeke, K. Wiśniewski, M. Grinberg, F. Rozpłoch 2002). The addition of alkali oxides as a modifier transforms some of $BO_3$ into four coordinated tetrahedral $BO_4$ units (Varshneya 1994). All spectra showed three, but rather broad, main bands characteristic for planar triangles $BO_3$ with a certain fraction of six-member rings (Vicente et al. 2014; Cz. Koepeke, K. Wiśniewski, M. Grinberg, F. Rozpłoch 2002) and four coordinated tetrahedral $BO_4$ units (Varshneya 1994) commonly found for alkali borate glasses. Such broadening is most likely due to the combination of highly degenerate vibrational states, thermal broadening of the lattice dispersion band, and mechanical scattering from powder samples. The first band (shaded in blue) ranged from 1600 to 1170 cm$^{-1}$ (centered at 1360 cm$^{-1}$) is correlated to the stretching vibrations of B–O–B bond in the trigonal $BO_3$ unit (Kesavulu et al. 2010; Naga Raju et al. 2006; ElBatal et al. 2009; Subhashini and Shashikala 2016). This band revealed a clear splitting into three separate features at ~1233 cm$^{-1}$ and (~1330 & 1415 cm$^{-1}$), which are due to the existence of two types of $BO_3$ units containing non-bridging oxygen (NBO) atoms at blue arrow and those connected to the glass network by all three oxygen atoms (free of NBO), respectively (Hassan et al. 2019). The NBO was found to slightly increase with $Cr_2O_3$ content. The recorded band at ~1500 cm$^{-1}$ is attributed to overlap between the triangles and the O–H bending vibration mode (Kesavulu et al. 2010; Naga Raju et al. 2006). The second

![FTIR spectra of all prepared samples. The blue and yellow shaded areas correspond to vibrations from $BO_3$ and $BO_4$ structural units, respectively. The arrows indicate the peak position of NBO](image-url)
Table 2  Assignment of FTIR vibrational bands present in all glassy samples

| Spectral region in (cm$^{-1}$) | Assignment                                                                 | Ref                                                                 |
|-------------------------------|-----------------------------------------------------------------------------|----------------------------------------------------------------------|
| 1150–1600                     | Asymmetric stretching vibrations of triangle BO$_3$                        | Kesavulu et al. (2010); Naga Raju et al. (2006); ElBatal et al. (2009); Hivrekar et al. (2017) |
| 1500                          | Overlap with the triangles band due to the O–H bending vibration mode       | Kesavulu et al. (2010); Naga Raju et al. (2006)                       |
| 780–1170                      | B–O rocking and stretching motion in BO$_4$ tetrahedral                    | Kesavulu et al. (2010); Naga Raju et al. (2006); ElBatal et al. (2009); Hivrekar et al. (2017) |
| 590–780                       | B–O–B symmetric bending of triangle vibrations                              | Kesavulu et al. (2010); Naga Raju et al. (2006); ElBatal et al. (2009); Hivrekar et al. (2017) |
| 540                           | B–O–B vibrations                                                           | Hassan et al. (2019); Subhashini and Shashikala (2016); Suresh et al. (2016) |
| 470                           | Cr–O in hexavalent state which is a network former with CrO$_4^{2-}$ form   | Hassan et al. (2018); Hassan et al. (2019); Narendrudu et al. (2017); Parminder Kaur et al. (2019) |
| Below 500                     | Li ion vibration                                                           | Hassan et al. (2018); Hassan et al. (2019); Ahmad and Nabhan (2019); Vijayakumar et al. (2015) |
main broad band (shaded in yellow) observed within the range 1170–780 cm\(^{-1}\) is attributed to B–O and B–O–B stretching and rocking motions associated with \(BO_4\) (Kesavulu et al. 2010; Naga Raju et al. 2006; ElBatal et al. 2009; Subhashini and Shashikala 2016). Likewise, the band splits into three features at \(\sim 870\) cm\(^{-1}\) and \(\sim 940 \text{ & } 1050\) cm\(^{-1}\), in correlation with \(BO_4\) units connected to barely affected \(NBO\) (black arrow) and to all four oxygen atoms, respectively (Hassan et al. 2019). The third band (shaded in blue) located in the region 780–590 cm\(^{-1}\), with center at 690 cm\(^{-1}\), is attributed to the bending mode of long chain structural unit of \((B_3O_7)^{5-}\) species (Kesavulu et al. 2010; Naga Raju et al. 2006; ElBatal et al. 2009; Subhashini and Shashikala 2016; Suresh et al. 2016; Hivrekar et al. 2017), i.e. boron atoms vibrate perpendicular to \(O_3\) plane of their triangles \(BO_3\). On the other hand, a weak feature is observed at \(\sim 540\) cm\(^{-1}\) which belongs to the B–O–B vibrations and/or borate ring deformations (Hassan et al. 2019; Moustafa and Hassaan 2017; Sousa et al. 2011). Below 500 cm\(^{-1}\) a band of Li ionic vibration is observed (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Vijayakumar et al. 2015). Finally, samples containing higher Cr concentration (e.g., \(x=0.3, 0.5\) mol%), exhibit weak feature at \(\sim 470\) cm\(^{-1}\) which belongs to vibrations of \(Cr^{6+}\) in \(Cr_4^{2-}\) structural units (Hassan et al. 2018, 2019; Narendrudu et al. 2017; Parminder Kaur et al. 2019). These fine features are easily seen in the zoom-in and deconvoluted spectra presented in Fig. 5a. The Cr and Li bands, identified after the deconvolution process, clearly increase with Cr ions concentration as depicted in Fig. 5b. Contrarily, the value of \(N_4\) (which quantifies the relative population of borate species) decreases from 46 to 38% with the concentration of \(Cr_2O_3\), while the \(NBOs\) are barely increased.

![Fig. 5](image-url) (Top) Deconvolution process for the \(x=0.5\) samples, in the low wavenumber side, showing \(Cr^{6+}\), Li, and B-O-B vibrations. (Bottom) Variation of \(N_4\), \(NBO\), and Li&Cr bands as a function of \(Cr_2O_3\) content. The length of the vertical arrows highlights the maximum observed change.
3.4 ESR Results

ESR spectra for 0.1, 0.2, 0.3 and 0.4 Cr-doped samples are presented in Fig. 6. The spectra were all normalized with respect to their mass to ensure a reasonable quantitative comparison. As evident from Fig. 6, there exist four resonances with effective g values 4.9 and 4.1, at low field, and 2.2 and 1.9, at high field. The two low field resonances with g = 4.9 and 4.1 are vastly reported to originate from isolated Cr$^{3+}$ ion sites of rhombic symmetry exposed to strong ligand field (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Padlyak et al. 2012; Ravikumar et al. 2005; Vijay Singh and Chakradhar 2009; Varshneya 1994; Schneider et al. 1996; Laxmi Kanth et al. 2005). The resonance signal observed at the effective value of $g = 2.2–2.3$ has been attributed to exchange coupled pairs of Cr$^{3+}$–Cr$^{3+}$ ions (Padlyak et al. 2012; Vijay Singh et al. 2014; Vijay Singh and Chakradhar 2009). The sharp resonance signal with effective $g = 1.9$ most likely arises due to Cr$^{5+}$ ions (i.e., the charge transfer state of Cr$^{6+}$) (Hassan et al. 2018, 2019; Ahmad and Nabhan 2019; Kesavulu et al. 2010; Terczynska-Madej et al. 2010; Little Flower et al. 2007). The intensity of this resonance increases, almost linearly, with increasing Cr content. However, the intensity dependence for the other three resonances on Cr concentration has non-monotonic behavior. The two low field resonances with effective $g$ values $g = 4.9$ and 4.1 follow quite similar behavior with Cr concentration, which indicates that the two signals have the same origin (i.e., Cr$^{3+}$ ions). The 0.3 Cr sample exhibits the strongest intensity deviation among this doping series, where the resonance for $g = 2.2–2.3$ is the most intense (shaded region) while the intensity for the other two low field signals at $g = 4.9$ and 4.1 are lowered. This may be attributed to the presence of large fraction of Cr$^{3+}$ ions exchange coupled in pairs for this sample. In fact, by considering the overall area under all Cr$^{3+}$ resonance, i.e., the two low field ($g = 4.9$ and 4.1) and the high field ($g = 2.2–2.3$) resonances, the average Cr$^{3+}$ contributions increases monotonically with Cr concentration.

Fig. 6 ESR spectra for all chromium doped samples. The color scale distinguishes resonance from Cr$^{3+}$(blue-red) and Cr$^{6+}$ (green) oxidation states
4 Conclusion

Chromium-doped borate glass systems of composition $x\text{Cr}_2\text{O}_3-(70-x)\ \text{B}_2\text{O}_3-30\ \text{Li}_2\text{O}_3$ with exceedingly small doping level ($x=0, 0.1, 0.2, 0.3$ and $0.5$ mol %) were prepared utilizing the melt quenching technique. For such a diluted Cr-doping, well-defined near-edge Cr$^{6+}$ optical transitions were unambiguously identified, and the optical band gap of the glass systems was precisely determined. Away from the absorption edge, specifically in the visible spectral regime, additional Cr$^{3+}$ transitions showed up thereby modulating the glass color from colorless to dark greenish with increasing Cr content. The existence of both Cr$^{6+}$ and Cr$^{3+}$ was ensured by measuring their oxidation states using electron spin resonance spectroscopy. The vibrational spectra for all samples were similarly dominated by borate characteristic groups, namely $\text{BO}_3$ and $\text{BO}_4$ structural units, while additional weak Cr$^{6+}$ vibrations are developed with Cr doping.

References

Abd El-Fattah, Z.M., Ahmad, F., Hassan, M.A.: J. Alloys Compd. 728, 773 (2017)
Ahmad, F.: J. Alloys Compd. 586, 605 (2014)
Ahmad, F., Nabhan, E.: Opt. Quant. Electron. 51, 261 (2019)
Akhshay, V.R., Arun, B., Mandalc, G., Vasundhara, M.: Phys. Chem. Chem. Phys. 21, 12991 (2019)
Chattree, K.K., Forster, L.S.: Spectrochim. Acta 20, 1603 (1964)
Dahshan, A., Saddeek, Y.B., Aly KHS Shaaban, K.A., Hussein, M.F., Abo El Naga, A.O., Shaban, S.A., Mahmoud, S.O.: J. Non-Cryst. Solids 508, 51 (2019)
Dattu Mote, V., Huse, V.R., Dole, B.N.: World J. Condens. Matter Phys. 2, 208 (2012)
Dubey, R.S., Singh, S.: Results Phys. 7, 1283 (2017)
Durga, D.K., Veeraiah, N.: Phys. B 324, 127 (2002)
El Batal, H.A., Abou Hussein, E.M., El Alaily, N.A., EzzEldin, F.M.: J. Non-Cryst. Solids 528, 119733 (2020)
ElBatal, F.H., Hamdy, Y.M., Marzouk, S.Y., Non-Cryst, J.: Solids 355, 2439 (2009)
Farouk, M., Slibi, D.-A., Abd El-Fattah, Z.M., Atallah, M., El-Sherbiny, M.A., Hassan, M.A.: Silicon (2021). https://doi.org/10.1007/s12633-020-00649-1
Giridhar, G., SreehariSastry, S., Rangacharyulu, M.: Phys. B 406, 4027 (2011)
Habib, I.Y., Tajuddin, A.A., Noor, H.A., Lim, C.M., Mahadi, A.H., Kumara, N.T.R.N.: Sci. Rep. 9, 9207 (2019)
Hassan, M.A.: J. Alloys Compd. 574, 391 (2013)
Hassan, M.A., Farouk, M., Kashef, L., Abullah, A.H., ElOkr, M.M.: J. Alloys Compd. 539, 233 (2012)
Hassan, M.A., Ahmad, F., Abd El-Fattah, Z.M.: J. Alloys Compd. 750, 320 (2018)
Hassan, M.A., Ebrahim, F.M., Moustafa, M.G., Abd El-Fattah, Z.M., El-Okr, M.M.: J. Non-Cryst. Solids 515, 157 (2019)
He, J.-J.: Shao-YiWu, Li-Juan Zhang, Yong-Qiang Xu, Chang-Chun Ding. J. Non-Cryst. Solids 437, 58 (2016)
Hivrekar, M.M., Sable, D.B., Solunke, M.B., Jadhav, K.M.: J. Non-Cryst. Solids 474, 58 (2017)
Kaur, Parminder, Singh, K.J., Kurudirek, Murat, Thakur, Sonika: Spectrochim. Acta A Mol. Biomol. Spectrosc. 223, 117309 (2019)
Kesavulu, C.R., Chakradhar, R.P.S., Jayasankar, C.K., Lakshmana Rao, J.: J. Mol. Struct. 975, 93 (2010)
Koepke, Cz., Wiśniewski, K., Grinberg, M.: J. Alloys Compd. 341, 19 (2002)
Koepke, Cz., Wiśniewski, K., Grinberg, M., Rozploch, F.: J. Phys.: Condens. Matter 14, 11553 (2002)
Lakshmana Rao, J., Sreedhar, B., Ramachandra Reddy, M., Lakshman, S.V.J.: J. Non-Cryst. Solids 111, 228 (1989)
Lakshmana Rao, B., Ravi Babu, Y.NCh., Prasad, S.V.G.V.A.: J. Non-Cryst. Solids 382, 99 (2013)
LaxmiKanth, C., Raghavaiah, B.V., Appa Rao, B., Veeraiah, N.: J. Quant. Spectrosc. Radiat. Transf. 90, 97 (2005)
Little Flower, G., Srinivasa Reddy, M., SahayaBaskaran, G., Veeraiah, N.: Opt. Mater. 30, 357 (2007)
