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Physical, optical and luminescence properties of zinc aluminium barium borate glasses doped with chromium oxide

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Abstract

Zinc aluminium barium borate glasses doped with Cr^{3+} ions at the composition of (60-x) B_2O_3:10ZnO:20BaO:10Al_2O_3:xCr_2O_3, where x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol%, have been synthesized by conventional melt quenching technique at 1,100 °C for 3 hours. The physical, optical and luminescence properties of zinc aluminium barium borate glasses were investigated. The results showed that density and molar volume of glass samples were in the range of 3.1682-3.2088g/cm^3 and 28.6672-29.9507 cm^3/mol, respectively. The optical absorption spectra of glasses were measured in the wavelength range of 200-2,500 nm. The intensity of all absorption bands increased with increasing Cr_2O_3 . ln addition, the luminescence properties of Cr^{3+} doped zinc aluminium barium borate glasses system were carried out using excitating wavelength of 347 nm and the luminescence peaks around 694 nm were observed.

Keywords: zinc borate glasses, chromium oxide, optical properties, luminescence properties

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1. Introduction

Glasses doped with transition metal ions still gather continuous interest as materials attractive for optoelectronic applications [1, 2]. These applications are based on the fact that ions in the glassy (vitreous) matrix are characterized by the optical properties typical for inhomogeneous broadening of the density of states [3]. This inhomogeneity can be a very attractive property addressed to such applications as optical memory media based on the spectral hole-burning [4], etc. Another branch of the possible optoelectronic applications is search for new tunable laser materials. Borate glasses may be considered as promising materials which can accept the transition metal and rare earth ions as efficient dopants [5, 6, 7].

B_2O_3 is one of the most important glass forming oxides and has been incorporated into various kinds of glass systems in order to attain the desired physical and chemical properties. Borate glasses have been of particular scientific interest for many years [8, 9, 10, 11, 12, 13, 14, 15]. Borate glasses have several commercial applications because of high thermal expansion coefficient, low melting point and softening temperature, high electrical conductivity and optical characteristics.

BaO contained glasses are very important due to their various applications such as, its suitability for liquid waste, making barrier of plasma display ribs, gamma ray shielding material, and crown optical glasses. [16].

Al_2O_3 doped with transition metal Cr^{3+} ion is the most important phase for laser hosts, possessing excellent emitting properties [17, 18, 19, 20]. Aluminum oxide (Al_2O_3) plays a key role in many technologies due to its remarkable physical properties, such as high melting point, hydrophobicity, high elastic modulus, high optical transparency, high refractive index of about 1.76 at 632.8 nm wavelength, thermal and chemical stability, low surface acidity, and fine optical and dielectric characteristics [21, 22, 23, 24]. It can act as a tunnelling barrier for novel magnetic sensors and for organic transistors because of its large band gap (8 eV) [25].

ZnO was widely used to improve the chemical stability of borate glasses. Furthermore, ZnO is well-known as an intermediate oxide in glass since Zn^{2+} has a large ion radius and an electronic configuration with 18 outer-shell electrons [26]. Zn^{2+} can either form ZnO_4 [27]. Or BO_3–O–Zn bridges via borate chains linkages in the glass network.

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Table 1 Physical property of zinc aluminum barium borate doped with Cr^{3+} ions glasses

Cr_2O_3 (mol %)	ρ(g/cm^3)	M_T (g/mol)	V_M (cm^3/mol)
0.01	3.1951	91.5948	28.6672
0.02	3.2088	92.4186	28.8016
0.03	3.1952	93.2424	29.1820
0.04	3.1708	94.0662	29.6664
0.05	3.1682	94.8900	29.9507

The purpose of this work is to develop green emission glass materials without rare earth materials. The physical, structural, optical and luminescence properties of Cr^{3+} ions in zinc aluminium barium borate glasses have been characterized.

2. Materials and methods

Glass samples with the formula (60-x)B_2O_3:10ZnO:20BaO:10Al_2O_3:xCr_2O_3 (ZABaB:Cr^{3+}) with x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol% were prepared by melt quenching technique. Required quantities of ZnO, Al_2O_3, $BaCO_3$, Cr_2O_3, H_3BO_3 were weighed separately in an electronic balance before being mixed thoroughly. The mixtures were calcined to remove vapor and then were melted in alumina crucible at 1,100 °C for 3 hr. in an electric furnace. The homogenized melt was poured onto a preheated graphite mould to avoid breaking of the sample due to thermal stress and pressed with another plate to get the square-shaped sample. In order to prevent breaks and cracks, these glass samples were immediately annealed at 500 °C for 3 hr. and then cooled slowly to room temperature. Finally, the glass samples were cut and finely polish to a dimension of 1.0 cm x 1.5 cm x 0.3 cm. The density was measured by the Archimedes method using distill water as an immersion fluid. The molar volume was calculated using the relation V_M = MT/ρ, where MT is the total molecular weight of the multi-component system given by;

$$M_T = AM_{(ZnO)} + BM_{(Al_2O_3)} + CM_{(BaO)} + DM_{(B_2O_3)} + EM_{(Cr_2O_3)} \quad (1)$$

where A, B, C, D and E are the mole fractions of the constituent oxides and $AM_{(ZnO)}$, $BM_{(Al_2O_3)}$, $CM_{(BaO)}$, $DM_{(B_2O_3)}$ and $EM_{(Cr_2O_3)}$ are the molecular weights of the different oxides for glasses prepared in this research. The amorphous nature of the prepared glasses were confirmed through X–ray diffraction studies using a Shimadzu XRD–6100 diffractometer. The scanning region of 2 angles was set from 10° to 80° with a step rate of 5°/min. The optical absorption spectra of the glasses sample were recorded in the range of 200-2500 nm using a UV–3600 Shimadzu UV–VIS–NIR spectrophotometer. The luminescence spectra measurements were carried out using Cary Eclipse Fluorescence spectrophotometer with 347 nm excitation of xenon flash lamp.

3. Results and discussion

3.1 Density and molar volume

The density and molar volume of glass is usually considered as an important physical parameter and any observed changes in density value directly indicate the differences in the selected glass chemical composition and in turn the glass network structure. The results are show that in the range of 3.1682 - 3.2088 g/cm^3 indicating that they are not dependent on the concentration of the densities are Cr_2O_3. The molar volume of the glass systems under study changes with Cr_2O_3 content in a specific manner (Figure 1). When Cr_2O_3 into was doped the borate glass network, the molar volume is inversely proportional to the density. The molar volume increase slightly with increasing the concentration of Cr_2O_3. Which is attributed to the increase in the number of non-bridging oxygen (NBOs). A further addition of Cr_2O_3 may accordingly result in an extension of the glass network, reflecting that the inter-atomic spacing is expanded.

3.2 X-ray diffraction

Figure 2 Shows the XRD patterns for (60-x) B_2O_3:10ZnO:20BaO:10Al_2O_3:xCr_2O_3 (ZABaB:Cr^{3+}) with x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol% glass samples. The XRD spectra show the broad sharp peaks indicating that the samples are amorphous structural in nature [28].

3.3 Absorption spectra

The optical absorption spectra observed at room temperature for zinc aluminum barium borate doped with Cr^{3+} (ZABaB:Cr^{3+}) glass samples are shown in Figure 3. The spectra exhibits one broad band at 640 nm. The observed bands are characteristic of Cr^{3+} ion in octahedral symmetry [29]. The band is assigned to the d–d transitions $^4A_{2g}$ (F) → $^4T_{2g}$ (F). The absorption intensity of the absorption band increases with the increase of Cr_2O_3 concentration.

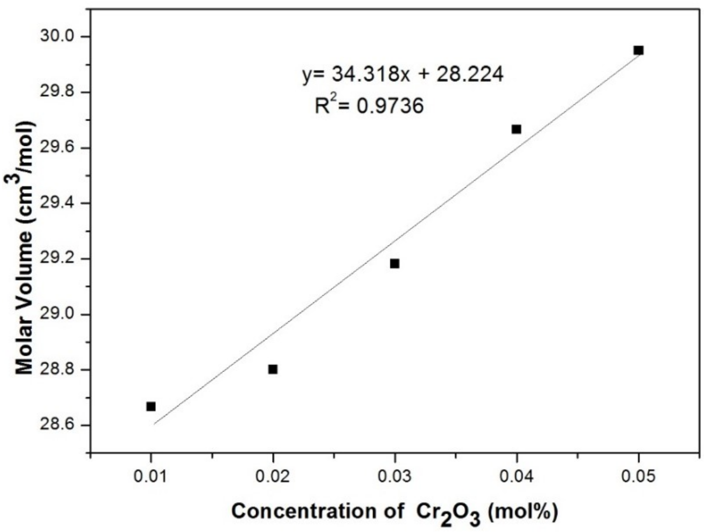

Figure 1 Molar volume of ZABaB:Cr^{3+}glass samples

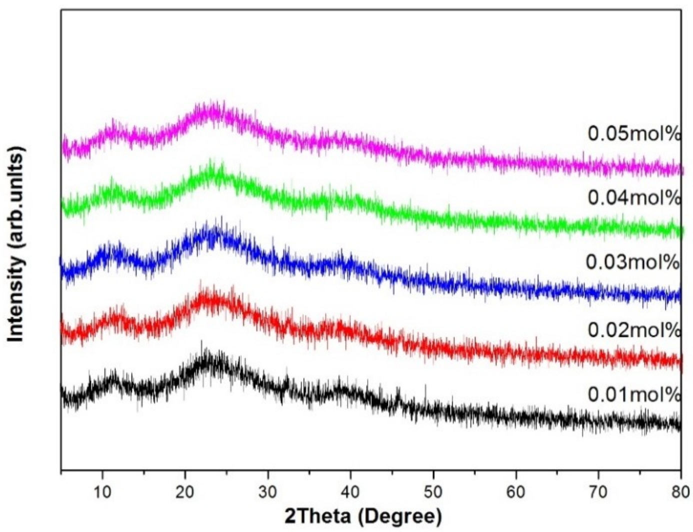

Figure 2 XRD patterns of ZABaB:Cr^{3+} glass samples with x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol%

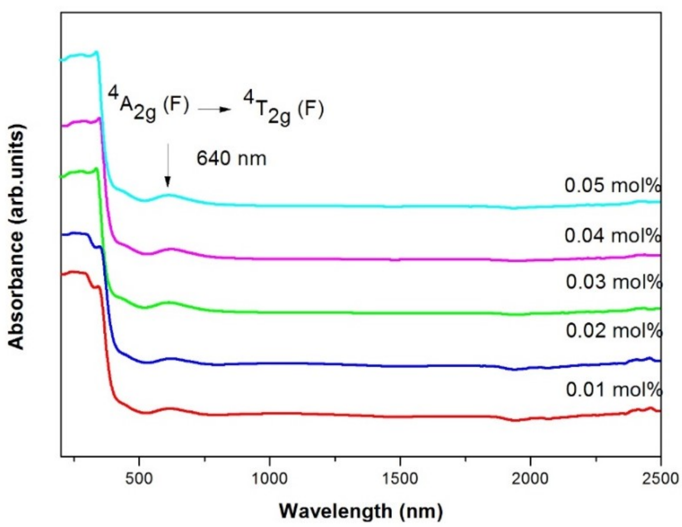

Figure 3 Optical absorption spectra of ZABaB:Cr^{3+} glass samples at room temperature

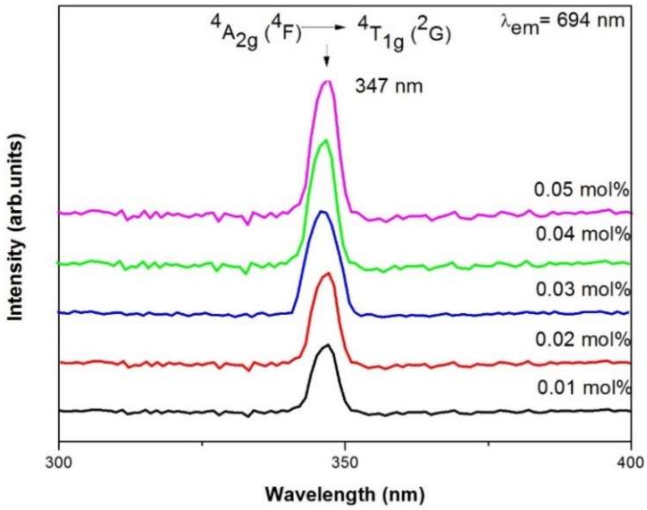

Figure 4 Luminescence excitation spectra of ZABaB:Cr^{3+}glass samples with x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol%

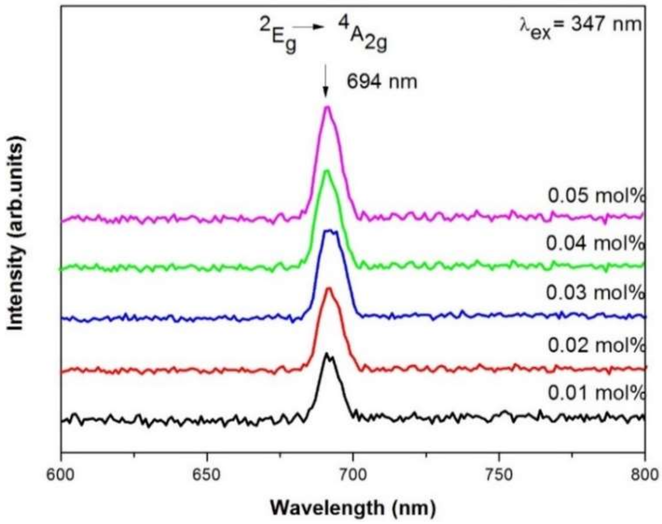

Figure 5 Luminescence emission spectra of ZABaB:Cr^{3+} glass samples with x = 0.01, 0.02, 0.03, 0.04 and 0.05 mol%

3.4 Luminescence spectra

The excitation spectra of zinc aluminnium barium borate glasses doped with Cr^{3+} (ZABaB:Cr^{3+}) were measured from 300-400 nm using the xenon flash lamp. One excitation peak was observed and assigned to the transition originating from the ground state, $^4A_{2g}$ (^4F) to the excited state $^4T_{1g}$ (^2G) (347 nm) of $Cr3^+$. The excitation spectra from 300-400 nm of Cr^{3+}doped in zinc aluminnium barium borate glasses are shown in Figure 4. Figure 5 shows the room temperature emission spectra recorded for all samples. One emission spectra of emission band corresponding to $^4T_{2g}$ (694 nm). The emission color is strongly dependent on the co-ordination environment of Cr^{3+} in the host matrix, and it emits a green light when it is octrahedrally co-ordinated (CN=6). The luminescence intensity of luminescence materials is known to be dependent on the doping concentration of luminescent ion. The energy level diagram for Cr^{3+} doped zinc aluminum barium borate glass can be presented as a diagram in Figure 6.

4. Conclusions

On the basis of the results reported in the present investigation, the following conclusions can be drawn:

4.1 The densities of the glass samples were in the range of 3.1682 – 3.2088 g/cm^3.

4.2 The molar volumes increase slightly with increasing the concentration of Cr_2O_3.

4.3 The XRD pattern confirm the amorphous nature of the prepared glasses.

4.4 The absorption spectra show a characteristic absorption band of Cr^{3+} at 640 nm which correspond to d-d transition $^4A_{2g}$ (F) → $^4T_{2g}$ (F).

4.5 The excitation spectrum occurs at 347 nm which due to the transition of $^4A_{2g}$ (^4F) → $^4T_{1g}$ (^2G).

4.6 The emission spectrum occurs at 694 nm which due to the transition of ^2E_g → $^4A_{2g}$.

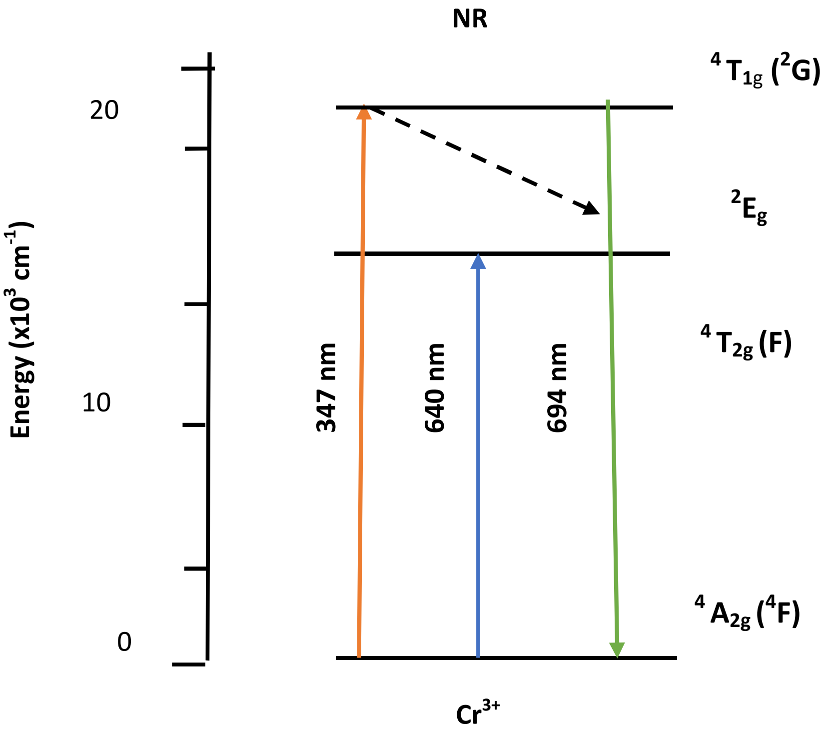

Figure 6 Diagram of partial energy levels of ZABaB:Cr^{3+}

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