PHOTOLUMINESCENCE AND OPTICAL PROPERTIES STUDY OF DY^{3+}-DOPED LITHIUM CALCIUM BORATE GLASSES

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Abstract

The preparation, optical and luminescence properties of Dy_2O_3 doped in lithium calcium borate glasses (LiCaB) with composition $50Li_2O$: 20CaO: (30-x)B_2O_3 : xDy_2O_3, where x = 0.00, 0.10, 0.30, 0.50, and 1.0 mol%. have been studied. The glasses were fabricated by normal melt quenching technique at 1000°C and then their properties were investigated. The optical spectra were measured and confirmed Dy^{3+} ions in glass matrices. The emission spectra of Dy^{3+}: LiCaB glasses exhibited 3 emission bands in the blue region at 483 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$), yellow region at 575 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$) and a weak band in red region at 665 nm ($^4F_{9/2} \rightarrow ^6H_{11/2}$) under the excitation at 388 nm. The peak intensities increase with the increase of concentration from 0.10 to 1.0 mol%.

Keywords: Borate Glass, photoluminescence, dysprosium

Introduction

Glasses are increasingly found in wide applications in modern science and technology due to their optical applications. For the past few decades throughout the world considerable laboratories concentrate on rare earth (RE) ions doped materials due to their potential applications in various fields like optoelectronics, lasers, fiber amplifiers, full-color display devices, optical data storage, white light emitting diodes and display monitors (Liu, *et al*., 2013; Sun *et al*., 2013; Swapnaa, *et al*., 2013; Zhang *et al*., 2014; Vijayakumar and Marimuthu, 2015). Borate-based glasses have many advantages, such as

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low cost, high stability and easy preparation; therefore, they have attracted very a great deal of interest from technological communities. As one kind of oxide glasses, borate glasses can easily prepared via traditional melt quenching technique (Mahamuda *et al.*, 2014; Venkataiah and Jayasankar, 2015). Borate glasses contain a dominant content of B_2O_3 as a glass former as adjustors which can modify the physical and chemical properties of the borate glasses. Borate glasses usually exhibit high solubility of RE ions, and the doping ions can be uniformly distributed in the borate glass that will to the ensure excellent optical and a great spectral performance. Among the various RE^{3+} ions, Dy^{3+} is one of the good luminescent ion which emits three visible bands, blue (470–480 nm; $^4F_{9/2}\rightarrow{}^6H_{15/2}$), yellow (570–580 nm; $^4F_{9/2}\rightarrow{}^6H_{13/2}$) and red (645–655 nm; $^4F_{9/2}\rightarrow{}^6H_{11/2}$) luminescence (Kiran and Suresh Kumar, 2013; Mahamuda *et al.*, 2014; Venkataiah and Jayasankar, 2015; Vijayakumar and Marimuthu, 2015)

In this study, the lithium calcium borate glasses (LiCaB) doped with europium ion (Dy^{3+}) were prepared by the normal melt quenching technique and investigate their physical, optical and luminescence properties for laser material applications.

Materials and Methods

The LiCaB: Dy^{3+} glass samples were synthesized with normal compositions $50Li_2O$:20CaO: $(30-x)B_2O_3$:xDy_2O_3 (where x = 0.0, 0.1, 0.3, 0.5 and 1.0 mol%). The powder mixtures were melted in an alumina crucible by normal melts quenching technique at 1000°C for about 3 h in an electric furnace. The melting was air quenched by pouring it into graphite molds and annealed at 450°C for 5 h to remove thermal strain. Then, the glass samples were taken to study the various properties. The densities were measured by the Archimedes method analysis with a densitometer (AND, HR-200) and molar volume was calculated using the relation $V_M = M_T/\rho$. The optical absorption spectra of the glass sample in the range of 450 – 2500 nm were recorded at room temperature with a Shimadzu UV-3600 UV-VIS spectrophotometer. The emission spectra measurements were carried out using Cary Eclipse Fluorescence Spectrophotometer with 388 nm excitation wavelength, the Commission International de L'Eclairage (CIE) standard.

Results

Physical Properties

Figure 1 shows LiCaB: Dy^{3+} glass samples of $50Li_2O$:20CaO:$(30-x)B_2O_3$:xDy_3O_3 (where x = 0.0, 0.1, 0.3, 0.5 and 1.0 mol%), respectively. All glass samples are transparent. The glass product was a light yellow. A clear and transparent as well.

Density and molar volume of the glass tends to increase the concentration of the compound of Dy_2O_3, as shown in Figure 2.

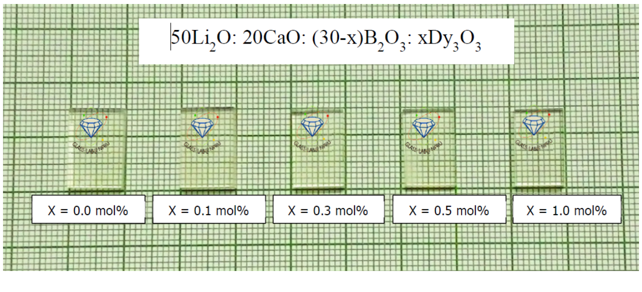

Figure1. Photograph of glass samples with where Dy_2O_3 concentration

Table 1 Physical property of glass samples prepared in the research

Glass samples where Dy^{3+} concentration (mol%)	Density (ρ) (g/cm^3)	Molar volume (cm^3/mol)
0.0	2.9272	16.0707
0.1	2.9307	16.1449
0.3	2.9348	16.3087
0.5	2.9537	16.3895
1.0	2.9750	16.7318

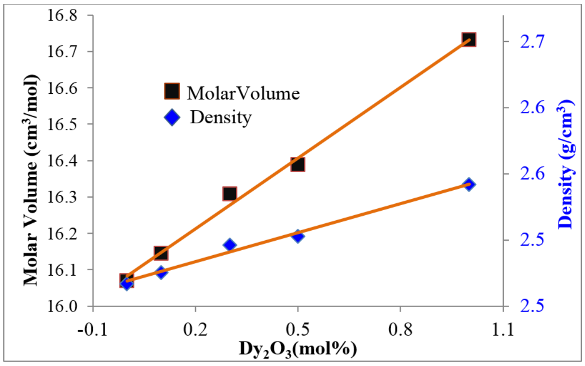

Figure 2. Density and Molar volume of glass samples with where Dy_2O_3 concentration

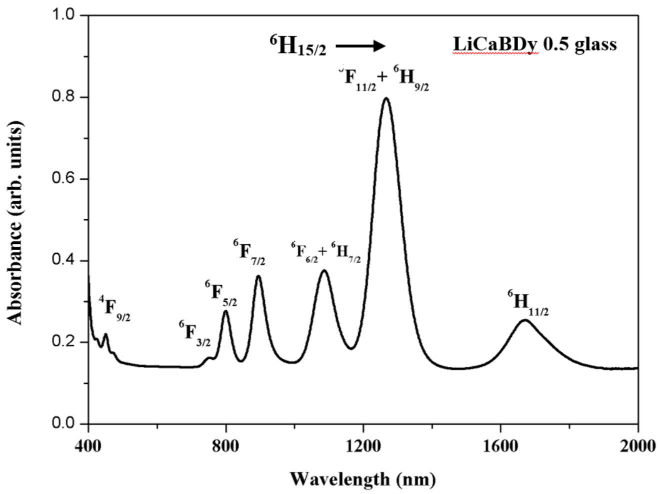

Figure 3. Absorption spectrum of LiCaBDy glass

Optical Properties

Absorption Spectra

Optical absorption spectrum of 0.5 mol% of Dy^{3+} ions doped glass recorded in the UV–VIS–NIR regions at room temperature is presented in Figure 3. The optical absorption spectrum exhibits seven bands centered at 450 nm, 748 nm, 797 nm, 898 nm, 1082 nm, 1263 nm and 1672 nm corresponding to the transitions from the ground state ($^6H_{15/2}$) to $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$+$^6H_{7/2}$, $^6F_{11/2}$+$^6H_{9/2}$ and $^6H_{11/2}$ respectively (Sun *et al*., 2013; Zhang *et al*., 2014; Vijayakumar and Marimuthu, 2015).

Figure 4 shows the room temperature emission spectra of LiCaB glasses doped with different concentrations of Dy^{3+} ions. However, we have also recorded the emission spectra for Dy^{3+} doped LiCaB glasses by fixing the excitation wavelength at 388 nm using a commercial Spectrophotometer (Kiran and Suresh Kumar, 2013; Liu, *et al*., 2013; Sun *et al*., 2013; Zhang *et al*., 2014; Vijayakumar and Marimuthu, 2015).

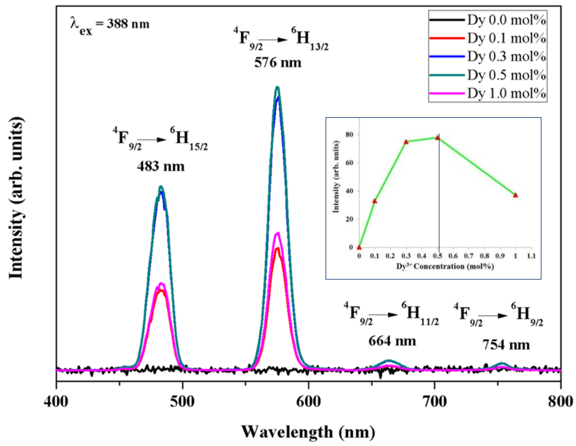

Figure 4. Luminescence spectra of Dy^{3+} ion doped LiCaB glasses

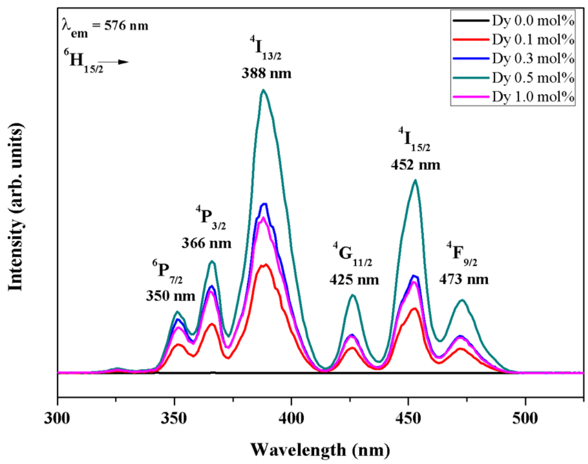

Figure 5. Excitation spectra of Dy^{3+} ion doped LiCaB glasses

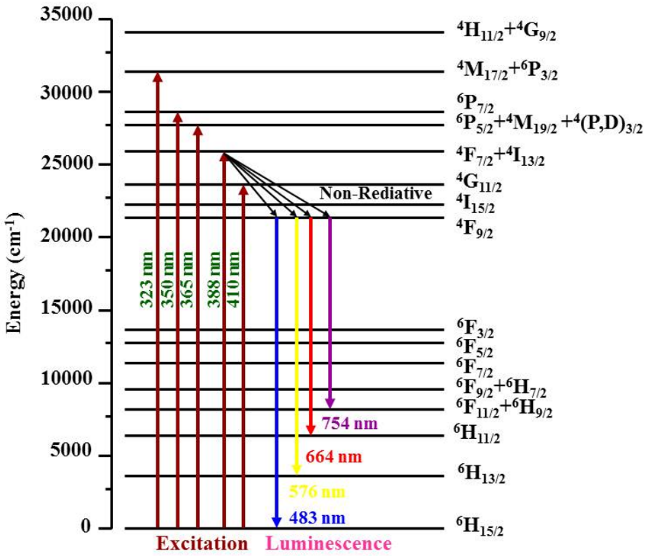

Figure 6. Partial energy level diagram of 0.5 mol% of Dy^{3+} ions in LiCaB glass (LiCaBDy0.5) with excitation and luminescence

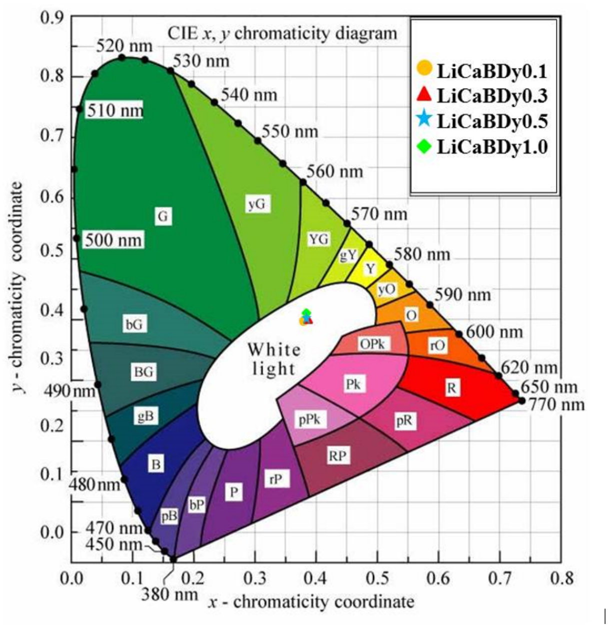

Figure 7. CIE coordinate diagram of LiCaB:Dy^{3+} glasses under 388 nm excitation

The inset in Figure 4 shows the emission spectra of Dy^{3+} doped LiCaB glasses at an excitation wavelength 388 nm. Both the emission spectra recorded exhibit four emission bands at 483, 576, 664 and 754 nm corresponding to $^4F_{9/2}$-$^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$ and $^6H_{9/2}$ transitions respectively. (Vijayakumar and Marimuthu, 2015). The partial energy level diagram shown in Figure 6 clearly explains the absorption, excitation and emission process observed in LiCaBDy 0.5 glass.

CIE chromaticity analysis

According to the Commission International de L'Eclairage (CIE) standard, the computed color coordinates (X; Y) for the 0.5 mol% of Dy^{3+} doped in LiCaB glasses are superimposed on the CIE chromaticity diagram to check the validity of the obtained results. The x and y coordinates were calculated as 0.3693 and 0.4073, respectively. From Figure 7, the emission color of Dy^{3+}: LiCaB glasses was white light (Mahamuda *et al*., 2014).

Conclusions

In summary, the developed Dy^{3+}-doped LiCaB glass was carried out through the photoluminescence and optical properties. The emission spectra showed four emissions (483, 574, 664 and 754 nm) for xDy^{3+}:LiCaB glass. Luminescence quenching has been experienced for glasses having Dy^{3+} ion concentration beyond 0.5 mol%. The optimal concentration is found to be 0.5 mol% Dy_2O_3. The strongest white light emission can be observed by the naked eyes in x = 0.1, 0.3, 0.5 and 1.0 glass. This result may potential to develop emission display and laser material applications.

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References

Swapnaa, K., Mahamuda, Sk., Srinivasa Rao, A., Jayasimhadri, M., Sasikala, T., and Rama Moorthy, L. (2013). Visible fluorescence characteristics of Dy^{3+} doped zinc alumino bismuth borate glasses for optoelectronic devices. Ceram Int., 39:8459.

Liu, H, Yu, L., and Li, F. (2013). Photoluminescent properties of Eu^{3+} and Dy^{3+} ions doped $MgGa_2O_4$ phosphors. J. Phys. Chem. Solids, 74(2):196-199.

Zhang, P., Yong-ping, Pu., Xiao-juan, Zhu., Han-yu, Zheng., Jiao-jiao, Zhao., Yu-rong, Wu., Yan-jie, Luo., and Yu-wen, Liu. (2014). Luminescence properties of Dy^{3+} doped and Dy^{3+}/Ce^{3+} co-doped $CaO–Al_2O_3–SiO_2–B_2O_3$ glass for LED applications. Ceramics International.

Sun, X.-Y., Wu, S., Liu, X., Gao, P., and Huang, S.-M. (2013). Intensive white light emission from Dy^{3+}-doped $Li_2B_4O_7$ glasses. J. Non-Cryst. Solids, 368:51-54.

Vijayakumar, M., and Marimuthu, K. (2015) Structural and luminescence properties of Dy^{3+} doped oxyfluoro-borophosphate glasses for lasing materials and white LEDs. J. Alloys Comp., 629:230-241.

Kiran, N., and Suresh Kumar, A. (2013). White light emission from Dy^{3+} doped sodium–lead borophosphate glasses under UV light excitation. J. Mol. Struct., 1054:6-11.

Venkataiah, G., and Jayasankar, C.K. (2015). Dy3+-doped tellurite based tungsten-zirconium glasses: Spectroscopic study. J. Molecular, 1084:182-189.

Mahamuda, Sk., Swapna, K., Packiyaraj, P., Srinivasa Rao, A., Vijaya Prakash, G. (2014). Lasing potentialities and white light generation capabilities of Dy^{3+} doped oxy-fluoroborate glasses. J. Lumin., 153:382-392.