Luminescence Properties of Dy³⁺-doped Lutetium-Calcium-Silico-Borate Glasses for White Light Emitting Applications

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Abstract

Lutetium-calcium-silico-borate glasses doped with various concentrations of dysprosium ions (Dy³⁺) have been fabricated. The amorphous nature of glasses has been confirmed by XRD technique. The luminescence properties have been studied throughout the emission spectra, the combination of blue and yellow emissions was shown for all the glasses and white light emission could be observed. The x, y coordinates of the prepared glasses pass through the white light region in the CIE 1931 diagram and are suitable for white light emitting devices.

Keywords: Dy³⁺ ion, Glasses, Luminescence.

1. Introduction

Recently, the research on rare earth doped materials is significant emphasis due to their potential applications in fields of laser technology, optoelectronic devices, fiber optic amplifiers, infrared to visible up-converters and phosphors⁽¹⁻⁴⁾. The design and development of optical devices suitable for the above applications is required in detailed on characterization of optical absorption and luminescence properties. These properties mostly depend on nature and type of local environment around the rare earth ions (REⁿ⁺) and on the phonon energies of the host materials.

Glasses doped with rare earth ions are proving to be luminescence materials as they have high emission efficiencies. These emissions correspond to 4f-4f and 4f-5d

electronic transitions in the REⁿ⁺. The 4f-4f transition gives an especially sharp fluorescence pattern from the UV to the infrared region. This is due to shield effects of the outer 5s and 5p orbitals on the 4f electrons. In recent years, glasses doped with rare earth ions have drawn much attention due to their potential applications in solid state lasers, optical amplifiers and three-dimensional displays^(1, 5-7). Therefore luminescence properties of rare earth doped different glass hosts are being prepared and investigated with the purpose to know their utility for luminescence applications. Various glassy materials such as fluoride, phosphate, fluorophosphate, borate, fluoborate and tellurite have been widely investigated to understand the effect of host glass on the lasing properties of rare earth ions⁽⁸⁾. In general, a host glass with low phonon energies decreases non-radiative relaxation rates and gives high quantum efficiencies, which are useful to design lasers and optical fiber amplifiers^(7, 9). Out of the 14 lanthanide elements, dysprosium in its trivalent state (Dy³⁺) is an efficient emitter in the visible region and it is the only ion that emits two intense colors which on mixing in suitable proportions yields white light^(5, 10-12). Further, the 1.3 μm emission of Dy³⁺ ion is useful for optical communication and up conversion emission in the blue region may be utilized for the development of blue lasers^(5, 11, 13-14).

The present work reports the systematic investigations of Dy³⁺ ions doped lutetium-calcium-silico-borate glasses. The luminescence properties and CIE 1931 chromaticity coordinates have been calculated as a function of Dy³⁺ ion concentration. The results obtained in the present work

have been discussed.

2. Experimental

2.1 Sample fabrication

A series of based-glass with the molar compositions of $25.0\text{Lu}_2\text{O}_3 : 10.0\text{CaO} : 10.0\text{SiO}_2 : (55.0-x)\text{B}_2\text{O}_3$ (was represented as LuCSB glass) has been prepared with various doping concentration of $x\text{Dy}_2\text{O}_3$, ranging from 0.0, 0.1, 0.3, 0.5 and 1.0 mol%. The nominal compositions of all glass samples here after were referred as LuCSB:0.0Dy, LuCSB:0.1Dy, LuCSB:0.3Dy, LuCSB:0.5Dy and LuCSB:1.0Dy. Following high purity analytical reagents: Lu_2O_3 , CaO , SiO_2 , H_3BO_3 and Dy_2O_3 were taken as raw materials in glass preparation process by using melt-quenching method. Each batch of 20 g of well-mixed chemicals was taken into high alumina crucible and was melted at 1500°C in and electric furnace for 3 hours. The homogenous melts were quenched by pouring on a preheated stainless steel mold. The transparent samples were annealed at 550°C for 3 hours, subsequently cooled down to room temperature to remove the residue strain. The samples thus prepared were cut into rectangular-shaped and optically polished to obtain uniform thickness with the dimensions of $1.0 \times 1.5 \times 0.3 \text{ cm}^3$ for further investigations.

2.2 Measurements

The amorphous nature of the prepared glass samples was confirmed by XRD technique, using Shimadzu X-ray Diffractometer XRD-6100 with $\text{CuK}\alpha$ radiation source. The absorption spectra were monitored under absorbance mode in UV-VIS and NIR regions in the wavelength of 300-1800 nm using UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu). The emission photoluminescence spectra of the Dy^{3+} -doped LuCSB glasses were recorded using Cary Eclipse fluorescence spectrophotometer with a

xenon flash lamp. The densities were measured according to the conventional Archimedes's principle with distilled water as an immersion liquid. All the measurements were carried out at room temperature. The other physical properties such as molecular weight and molar volume were also calculated using the relevant expressions reported in our previous work⁽¹⁵⁾ and the results are represented in Table 1.

3. Results and discussion

3.1 XRD analysis

X-ray Diffractometer scans were taken to measure the glassy nature for all the glasses. The typical XRD profile of the LuCSB glass doped with 1.0 mol% of Dy_2O_3 is shown in Figure 1.

From this Figure, the XRD pattern does not exhibit and detectable sharp characteristic peak, but the broad diffused scattering occurs at the lower angles which indicates the glass sample is amorphous in nature and has non-crystalline structure. Remaining the glass samples also exhibit similar in nature, so they are not shown for other glasses in Figure 1.

Fig. 1. The typical XRD profile of LuCSB:1.0Dy glass.

Table 1. Some physical properties of Dy^{3+} -doped LuCSB glasses.

Physical properties	Glass samples				
	LuCSB:0.0Dy	LuCSB:0.1Dy	LuCSB:0.3Dy	LuCSB:0.5Dy	LuCSB:1.0Dy
Average molecular weight (g/mol)	149.3902	149.6936	150.3004	150.9071	152.4240
Density (ρ) (g/cm ³)	2.0335	2.0790	2.1161	2.1634	2.2543
Molar volume (V_M) (cm ³ /mol)	73.4649	72.0024	71.0284	69.7545	67.6148

 Fig. 2. The absorption spectra of Dy³⁺-doped LuCSB glasses.

3.2 Absorption spectra

The optical absorption spectra of Dy³⁺-doped LuCSB glasses in the UV-VIS and NIR regions are shown in Figure 2(a) and 2(b), respectively. The absorption spectra of the all glasses were found to be alike with slightly difference in their intensity. From observation, the absorption intensity of the all bands increased with the increasing of Dy₂O₃ concentration. The spectra consist of inhomogeneous absorption bands due to the transitions assigned from ground state, ${}^6\text{H}_{15/2}$ to various excited states of Dy³⁺ ions.

In this present work, the absorption spectrum of Dy³⁺ ions shows totally twelve absorption bands located at 324, 349, 362, 386, 451, 474, 744, 794, 885, 1082, 1255 and 1645 nm are observed which are assigned to ${}^6\text{H}_{15/2} \rightarrow {}^4\text{D}_{7/2}$, (${}^4\text{M}_{15/2} + {}^6\text{P}_{7/2}$), ${}^4\text{P}_{3/2}$, ${}^4\text{F}_{7/2}$, ${}^4\text{I}_{15/2}$, ${}^4\text{F}_{9/2}$, ${}^6\text{F}_{3/2}$, ${}^6\text{F}_{5/2}$, ${}^6\text{F}_{7/2}$, ${}^6\text{F}_{9/2}$, (${}^6\text{H}_{9/2} + {}^6\text{F}_{11/2}$) and ${}^6\text{H}_{11/2}$ transitions, respectively. The observed band positions are found to be same irrespective of the change in glass position and the band assignments were compared with a standard wavelength chart for the Dy³⁺ ion and do supports the previous related studies^(5, 16-17).

3.3 Luminescence spectra

The luminescence behavior of Dy³⁺-doped LuCSB glasses have been studied throughout the emission spectral measurement. The luminescence spectra have been recorded by monitoring an excitation at 388 nm as a function of various Dy³⁺ ion concentrations and are shown in Figure 3. The mainly three emission luminescence bands corresponding to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_J$ (J = 15/2, 13/2 and 11/2) transitions located the same wavelength nearly at 481 nm (blue), 575 nm (yellow) and 664 nm (red) are observed, in spite of change in concentration. From Figure 3, it is also indicates that the luminescence intensity increases along with increase in Dy³⁺ ion concentration. Among the three emission bands, the band at ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ is magnetic dipole (MD) transition possessing the most intense, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition possessing moderate intensity, which is related to electric dipole (ED) transition, and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ transition possessing the lowest intensity^(6-7, 9).

Fig. 3. The emission spectra of Dy³⁺-doped LuCSB glasses.

Fig. 3. The partial energy level diagram of Dy³⁺ ions showing the possible emission transitions and non-radiative (NR) decay in Dy³⁺ doped LuCSB glasses^(7, 18).

3.4 Color coordinates

From emission spectra in Figure 3, the Dy³⁺ doped LuCSB glasses having important emissions in blue (481 nm) and yellow (575 nm) regions. The appropriate combination of blue and yellow light can generate white light emission. In order to find out color coordinates for all the glasses, the emission spectra have been characterized by the CIE 1931 chromaticity diagram⁽⁶⁾. The color of the luminescent source can be described by three color matching function parameters, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$, which are the dimensionless parameters^(6, 18). For a given power spectral density $P(\lambda)$, the degree of stimulation required to match the color of $P(\lambda)$ is express by⁽¹⁸⁾

$$X = \int \bar{x}(\lambda) P(\lambda) d\lambda \quad (1)$$

$$Y = \int \bar{y}(\lambda) P(\lambda) d\lambda \quad (2)$$

$$Z = \int \bar{z}(\lambda) P(\lambda) d\lambda \quad (3)$$

Where X , Y and Z are the tristimulus values which gives the power for each of the three primary colors to match with the color of $P(\lambda)$ and from the tristimulus values the color chromaticity coordinates x and y can be calculated using the following expression⁽¹⁸⁾

$$x = \frac{X}{X + Y + Z} \quad (4)$$

$$y = \frac{Y}{X + Y + Z} \quad (5)$$

The estimated CIE chromaticity coordinate values (x, y) for all the glasses are presented in Table 2. All the samples possess the chromaticity coordinates lies within the white light region. From this result, it is suggested that the all glass samples can be used as white light emitting devices.

Table 2. The chromaticity color coordinates of Dy³⁺-doped LuCSB glasses.

Samples	x	y
LuCSB:0.1Dy	0.369	0.405
LuCSB:0.3Dy	0.368	0.404
LuCSB:0.5Dy	0.369	0.405
LuCSB:1.0Dy	0.368	0.405

Fig. 4. The typical color chromaticity diagram of LuCSB:1.0Dy glass.

4. Conclusions

The Dy³⁺-dope lutetium-calcium-silico-borate based glasses have been fabricated and characterized their properties through, absorption spectra, emission spectra and CIE 1931 color chromaticity studies. The amorphous nature of the glasses was confirmed by XRD technique. With increasing of Dy³⁺ ions concentration, the densities were increased due to the high relative molecular mass of Dy₂O₃ compared to other glass constituents. While the additional of Dy₂O₃ leads to the decrease of the molar volume due to the increase of bond strength between atoms.

The luminescence spectra exhibited three emission bands corresponding to ⁴F_{9/2} → ⁶H_{15/2} (481 nm), ⁴F_{9/2} → ⁶H_{13/2} (575 nm) and ⁴F_{9/2} → ⁶H_{11/2} (664 nm) transitions under 388 nm excitation. The estimated CIE chromaticity coordinates fallen within white light region, suggesting all glasses could find applications as white light emitting materials.

Acknowledgment

The authors are grateful to National Research Council of Thailand (NRCT) for providing financial support this research.

References

- (1) E. Malchukova, B. Boizot, D. Ghaleb and G. Petite, "Optical properties of pristine and γ -irradiated Sm doped borosilicate glasses", Nuclear Instru. Methods Phys. Res. A, Vol. 537, pp. 411-414, 2005.
- (2) F. Vetrone, J.C. Boyer, J.A. Capobianco, A. Sepghini and M. Bettinelli, "980 nm excited upconversion in an Er-doped ZnO-TeO₂ glass", Appl. Phys. Lett., Vol. 80 pp. 1752-1754, 2002.
- (3) P.R. Biju, G. Jose, V. Thomas, V.P.N. Nampoory and N.V. Unnikrishnan, "Energy transfer in Sm³⁺:Eu³⁺ system in zinc sodium phosphate glasses", Opt. Mater., Vol. 24, pp. 671-677, 2004.
- (4) G. Lakshminarayana, R.Y. Mengfei and J. Qiu, "Spectral analysis of RE³⁺ (RE = Sm, Dy, and Tm): P₂O₅-Al₂O₃-Na₂O glasses", Optical Materials, Vol. 31, pp. 1506-1512, 2009.
- (5) D. Rajesh, Y.C. Ratnakaram, M. Seshadri, A. Balakrishna and T.S. Krishna, "Structural and luminescence properties of Dy³⁺ ion in strontium lithium bismuth borate glasses", J. Lumin., Vol. 132, pp. 841-849, 2012.
- (6) S. Babu, V. Reddy Prasad, D. Rajesh, and Y.C. Ratnakaram, "Luminescence properties of Dy³⁺ doped different fluoro-phosphate glasses for solid state lighting applications", J. Mol. Struct., Vol.1080, pp. 153-161, 2015.
- (7) N. Vijaya, K. Upendra Kumar, and C.K. Jayasankar, "Dy³⁺-doped zinc fluorophosphate glasses for white luminescence applications", Spectrochim. Acta, Part A, Vol. 113, pp. 145-153, 2013.
- (8) R. Vijayakumar, G. Venkataiah, K. Marimuthu, "Structural and luminescence studies on Dy³⁺ doped boro-phosphate glasses for white LED's and laser applications", J. Alloys Compd., Vol. 652, pp. 234-243, 2015.
- (9) K. Venkata Rao, S. Babu, G. Venkataiah and, Y.C. Ratnakaram, "Optical spectroscopy of Dy³⁺ doped borate glasses for luminescence applications", J. Mol. Struct., Vol. 1094, pp. 274-280, 2015.
- (10) Pan-pan Zhang, Yong-ping Pu, Xiao-juan Zhu, Han-yu Zheng, Jiao-jiao Zhao, Yu-rong Wu, Yan-jie Luo and Yu-wen Liu, "Luminescence properties of Dy³⁺ and Dy³⁺/Ce³⁺ co-doped CaO-Al₂O₃-SiO₂-B₂O₃ glass for LED applications", Ceramic International, Vol. 41, pp. S729-S733, 2015.
- (11) B. Shanmugavelu and V.V. Ravi Kanth Kumar, "Luminescence studies of Dy³⁺ doped bismuth zinc borate glasses", J. Lumin., Vol. 146, pp. 358-363, 2014.
- (12) T. Sasikala, L. RamaMoorthy, A. Mohan Babu and T. Srinivasa Rao, "Effect of co-doping Tm³⁺ ions on the emission properties of Dy³⁺ ions in tellurite glasses", J. Solid State Chem., Vol. 203, pp. 55-59, 2013.
- (13) K. Brahmachary, D. Rajesh and Y.C. Ratnakaram, "Luminescence properties of Dy³⁺ doped zinc-aluminum-sodium-phosphate (ZANP) glasses for white light applications", Optik, Vol. 126, pp. 4050-4055, 2015.
- (14) N. Kiran and A. Suresh Kumar, "White light emission from Dy³⁺ doped sodium-lead borophosphate glasses under UV light excitation", J. Mol. Struct., Vol. 1054-1055, pp. 6-11, 2013.
- (15) P. Chimalawong, K. Kirdsiri, J. Kaewkhao and P. Limsuwan, "Investigation on the physical and optical properties of Dy³⁺ doped soda-lime-silicate glasses", Procedia Engineering, Vol. 32, pp. 690-698, 2012.
- (16) G.H. Dieke, Spectra and Energy Levels of Rare-Earth

Ions in Crystals, New York: John Wiley & sons, 1969.

- (17) K. Swapna, Sk. Mahamuda, A. Srinivasa Rao, M. Jayasimhadri, T. Sasikala and L. Rama Moorthy, "Optical absorption and luminescence characteristics of Dy^{3+} doped Zinc Alumino Bismuth Borate glasses for lasing materials and white LEDs", J. Lumin., Vol. 139, pp. 119-124, 2013.
- (18) M. Vijayakumar and K. Marimuthu, "Structural and luminescence properties of Dy^{3+} doped oxyfluoroborophosphate glasses for lasing materials and white LEDs", J. Alloys Compd., Vol. 629, pp. 230-241, 2015.