Available Online at http://www.recentscientific.com

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 10, Issue, 06(E), pp. 33051-33056, June, 2019

ISSN: 0976-3031

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

OPTICAL AND LUMINESCENCE PROPERTIES OF SM3+ (0.5%) DOPED BAO-B2O3 GLASS

Ch.Vijay Anil Dai[1], Ch.Srinivasu[2], K.Suresh[3], T.Niranjan Kumar[4] and KVR Murthy[5]

[1]Department of Physics, AG & SG Siddartha College of Arts & Sciences, Vuyyuru
[2]Department of Physics, Andhra Loyola College, Vijayawada, A.P., India
[3]Department of Physics, VSR & NVR College, Tenali-522 201, A.P., India
[4]Department of Physics, AMAL College Anakapalli, Visakhapatnam, Andhra Pradesh
[5]Department of Applied Physics, Faculty of Engineering and Technology,
M.S.University of Baroda, Vadodara, Gujarat, India

DOI: http://dx.doi.org/10.24327/ijrsr.2019.1006.3595

ARTICLE INFO

Article History:
Received 4th March, 2019
Received in revised form 25th April, 2019
Accepted 18th May, 2019
Published online 28th June, 2019

Key Words:

Samarium, glass, annealing, melt-quenching, optical, luminescence

ABSTRACT

Binary glasses with the composition 40BaO-(60-x) B2O3: x Sm2O3 for x = 0 and 0.5 mol % were prepared by the melt-quenching technique. The prepared glass samples were characterized by optical absorption and photoluminescence spectra were recorded at room temperature. From the optical absorption studies it is found that five transitions from 6H5/2 → 4I11/2, 6P5/2, 6P3/2, 6P7/2 and 4D3/2 were observed at wavelengths 486 nm, 401 nm, 375 nm, 360 nm and 343 nm respectively. From the observed absorption edges optical band gap, the Urbach energies were calculated. The luminescence spectra exhibited conventional orange -red emission bands at around 563 nm, 600 nm, 647nm and 712nm corresponds to the 4G5/2 → 6H5/2, 6H7/2, 6H9/2 and 6H11/2 transitions respectively. The emission spectrum was observed under various excitation wavelengths. The emission spectrum measured is characterized through Commission International d'Eclairage (CIE) 1931 chromaticity diagram to explore its suitability for display and w-LED applications.

INTRODUCTION

Glass is a network of atoms bonded to each other through covalent bonds with oxygen atoms. It is usually tetrahedral bonded together in a random arrangement. The glass transition from solid glass to the viscous liquid glass is an important property. Basically glass is an elastic solid below the transformation region and a viscous liquid above it. The structure of the solid has all the attributes of a liquid except that solid does not flow on any meaningful time scale. If glass is cooled from the melt faster, the overall glass structure will have a large volume (lower density) than one that is cooled slowly. Glass is an elastic solid without the structural periodicity and long range order of crystalline material. It looks like a liquid but behaves like a solid.

Recent development of optical devices was based on rare earth ions doped materials is one of the interesting field of research. Rare earth doped glasses were used as optical device materials, sensors, solar concentrators, flat panel displays, fluorescent lamps, white LED's etc. [1-4]. 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 rare earth^{n+}. The 4f-4f transition gives sharp fluorescence pattern from the UV to the infrared region. This is due to shield effects of the outer 5s and 5p orbital's on the 4f electrons [5]. The lanthanum group doped materials is important because of their potential applications in the fields of optical device technology, optoelectronic devices, infrared to visible up-converters and phosphors [6].

Glasses are attractive materials in these applications as their ability to be cast in large and optically homogeneous pieces resulting in reduced cost. Over the past few years, there has been a considerable interest in the study of borate based glasses due to their structural and optical properties.

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. When alkaline or alkaline earth cations are introduced in the borate glass matrix, more structural variations can be observed.

Corresponding author:* **Ch.Vijay Anil Dai
Department of Physics, AG & SG Siddartha College of Arts & Sciences, Vuyyuru

Samarium containing borate glasses are known to have an unusual elastic behavior due to valence instability [7]. Samarium exhibits promising characteristics for spectral hole burning studies [8, 9]. Sm^{3+} ions are important activators for inorganic lattices, giving rise to the emission of reddish orange light due to electronic transitions $^6G_{5/2}\rightarrow{}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$. Sm^{3+} ions act as spectroscopic probe of local structure around rare earth ions in condensed matter due to electric dipole character of $^4G_{5/2}\rightarrow{}^6H_{5/2}$ hypersensitive transition, whose intensity increases as the environmental symmetry of the luminescence site decreases [10]. However, the studies on samarium containing glasses have received relatively less attention than the other lanthanides, despite many features of interest.

Recently, Hager *et al.* [11] studied luminescence spectra and optical properties of TeO_2–WO_3–Li_2O glasses doped with Sm ions. Eariah *et al.* [12] reported optical properties of samarium doped zinc phosphate glasses. Venkateswarlu *et al.* [13] studied influence of mixed alkalies on spectroscopic parameters of Sm^{3+} doped chloroborate glasses. Structural and luminescence investigations on Sm^{3+} doped sodium fluoroborate glasses containing alkali/alkaline earth metal oxides were reported by Arul Rayappan *et al.* [14]. Effect of CdS nanoparticles on fluorescence from Sm^{3+} doped SiO_2 glass has been reported by Rai *et al.* [15]. Though considerable research work on Sm^{3+} doped glasses are available in literature, no attempt has been made on spectroscopic investigations of Sm^{3+} (0.5%) doped barium borate simple glass matrix.

In the present work, synthesis, optical and luminescence properties of barium borate glasses doped with Sm named here after as SbBSm0 and SbBSm0.5, characterized through optical absorption, excitation and emission spectral measurements were done. The characteristics of the emission color were examined through CIE 1931 chromaticity diagram.

MATERIALS AND METHODS

Glasses Preparation

The glass samples were prepared by the standard melt quenching method with the following compositions. 40BaO-(60-x)B_2O_3: xSm_2O_3 where x= 0 and 0.5 mol%. About 10 gm of the batches of composition were taken and grounded completely in an agate mortar to get homogenised mixture. The homogeneous mixture was then taken into a silica crucible and heated at 1000°C in an electrical furnace for 10 min until the homogeneous melt was obtained. This soften was then poured quickly on a brass mildew and ironed quickly with another brass mildew to get circular formed glass samples with uniform thickness. The glass samples thus prepared were annealed at 400°C in order to make them free from thermal strains.

Measurements

The optical absorption spectra were recorded on a JASCO UV-VIS-NIR spectrophotometer (model V-670) at room temperature within the range 200–2000 nm with a scanning speed 100nm/min. The emission and excitation spectra for all the prepared glasses were recorded at room temperature using Shimadzu RF-5301 PC-Spectrofluorophotometer with a spectral resolution 0.5 nm. CIE colour co-ordinates were drawn using Radiant Imaging software version 2.0.

RESULTS AND DISCUSSION

Optical absorption spectra and energy level analysis

The room temperature optical absorption spectrum in the UV-VIS region of BaBSm0 and BaBSm0.5 glasses are shown in Fig. 1(a) and 1(b) respectively. The spectra consist of SbBSm0 sample does not show any absorption bands where as SbBSm0.5 sample shows in homogeneous absorption bands.

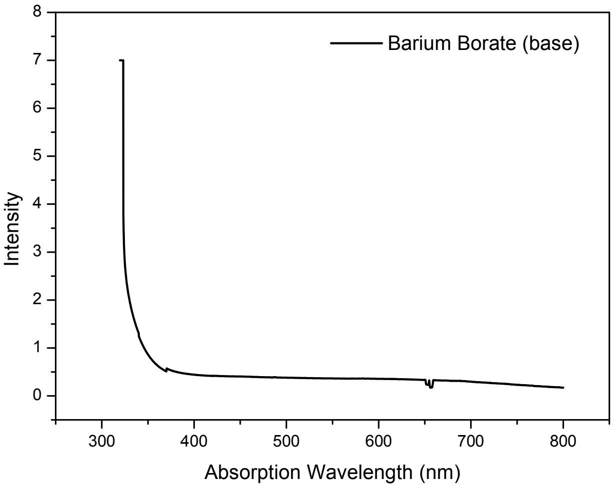

Figure 1(a) Optical absorption spectra of BaBSm0 glass sample

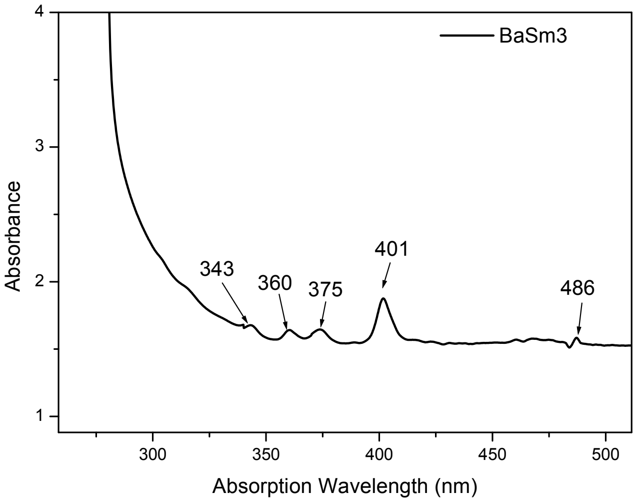

Figure 1(b) Optical absorption spectra of BaBSm0.5 glass sample

The room temperature optical absorption spectra of the prepared Sm^{3+} doped barium borate glasses consist of several in-homogeneously broadened bands of varying intensities. These bands correspond to the characteristic f-f transitions from the ground state $^6H_{5/2}$ of Sm^{3+} ions to their various excited states. The optical absorption spectra of the prepared glasses in the UV-Vis range (250 nm - 550 nm), recorded at room temperature is shown in Fig. 1(b). The band assignments were made with reference to the work by Carnall *et al.* [16] and Jaya shankar and Babu [17]. For the present glass series, five transitions from $^6H_{5/2}\rightarrow{}^4I_{11/2}$, $^6P_{5/2}$, $^6P_{3/2}$, $^6P_{7/2}$ and $^4D_{3/2}$ were observed at wavelengths 486 nm, 401 nm, 375 nm, 360 nm and 343 nm respectively. The absorption transitions are similar to those reported in other Sm^{3+} doped glasses [12, 15]. These bands are belongs to high energy group (350 nm-600 nm) in the UV-Vis region. It becomes difficult to assign the transitions in the UV-Vis region because of the overlapping of various (2S+1)L_J levels.

Band gap and Urbach's energy analysis

The optical band gap is a vital parameter within the field of photonics which provides data regarding the electronic structure of amorphous materials. The band gap energy values (E_{opt}) of the crystalline, amorphous materials are often evaluated with the help of the fundamental absorption edges through direct and indirect allowed transitions. The Mott and Davis theory was used to derive a relation between the band gap and the coefficient of absorption (α) and also the same is expressed using the equation, $(\alpha h\upsilon)^n = B(E-E_g)$ where α is the absorption coefficient, E is the energy of the applied photon, h is the plank's constant, υ is the frequency of the applied photon, B is the band tailing parameter, E_g is the band gap and n is equal to 2 or 1/2 which signifies direct or indirect allowed transitions. The graphs plotted between E and $(\alpha h\upsilon)^n$ referred as Tauc's plot and Tauc's plot for the title glasses. The linear portions of the Tauc's plot are often workout to zero absorption and also the intersection of E provides the optical band gap value.

A typical plot of $(\alpha h\upsilon)^2$ versus hυ for the glass having 40% BaO - 60% B_2O_3 named as BaBSm0 is presented in Figure 2(a). Extrapolation of this plot to $a^2 = 0$ provides the optical band gap E_g for direct transition. We have estimated the optical band gap value 3.4 eV for direct transition. The value of E_g for indirect transition is obtained by extrapolation of $(\alpha h\upsilon)^{1/2}$ versus hυ plot to $a^{1/2} = 0$ as shown in the Figure 2(b). We have estimated the optical band gap value 3.22 eV for indirect transition.

Figure 3(a) and 3(b) are the direct and indirect bandgap values of BaBSm0.5 glass. Estimated optical band gap value 4.4 eV for direct transition and estimated the optical band gap value 4.35 eV for indirect transition .This can be attributed to the structural changes that are taking place with the introduction of rare earth ions. Inclusion of rare earth ions in borate structure may create some defect states in the midgap, which is responsible for the decrease of bandgap. The broadness of the absorption edge may be due to the presence of localized state in the band tails. The calculated band gap values of the prepared glass are presented in table 1**.**

The Urbach energy 'E' which indicates the width of the band tails of the localized states and depends on temperature, induced disorder, static disorder and on average photon energies. Hence, Urbach energy provides a measure for the disorder in amorphous and crystalline materials. The nature of disorder is different for crystalline and amorphous solids. In amorphous solids, the static atomic structural disorder dominates and can be due to presence of defects like dangling bonds or non-bridging oxygens in glasses. Urbach energies (ΔE) are calculated by taking the reciprocals of the slopes of linear portion in the lower photon energy regions of the curves as shown in Figures 3(a) & 3(b). It shows the structural disorder of the system. Smaller is the value of Urbach energy, greater is the structural stability of the glass system. It is observed that the BaBSm0.5 glass has low value of structural disorder, which indicates the strong structural stability.

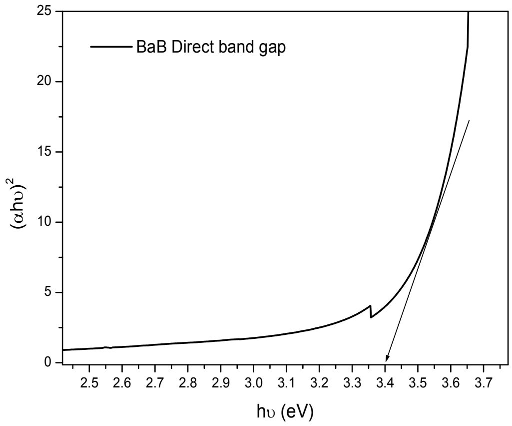

Figure 2(a) Direct bandgap BaB glass

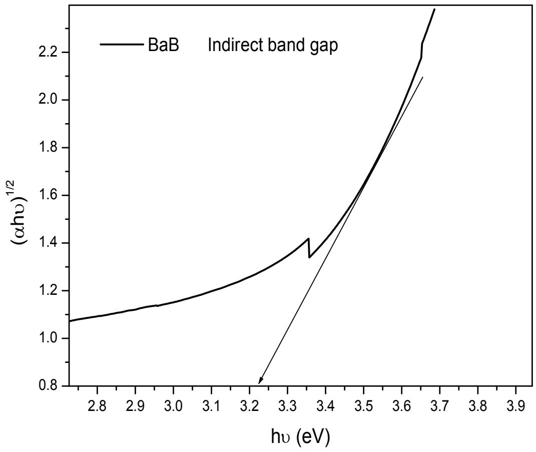

Figure 2(b) Indirect bandgap BaB glass

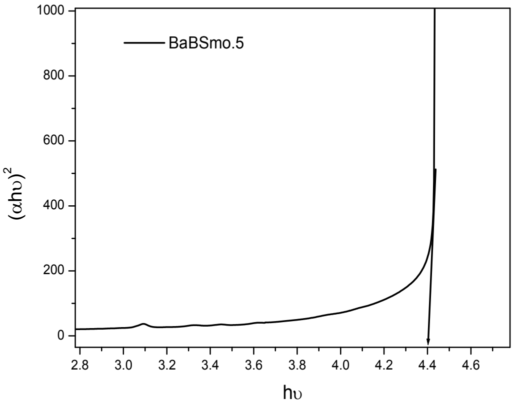

Fig 3(a) Direct Bandgap of BaBSm0.5 glass

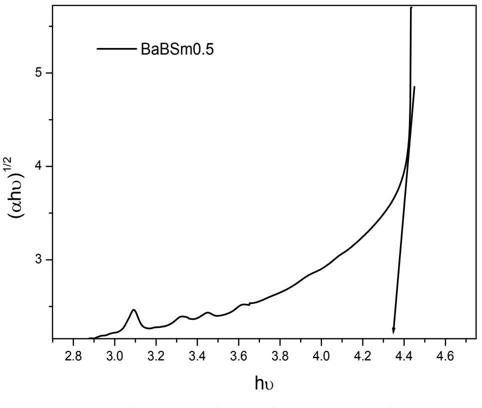

Fig 3(b) Indirect Bandgap of BaBSm0.5 glass

Table 1 The fundamental absorption edge (λ_{edge}), Optical band gap (E_{opt}) and Urbach's (ΔE) energy of the Sm^{3+} ions doped barium borate glass

S.No	Name of the glass	Absorption Edge(nm)	Optical Bandgap E (eV)		Urbach Energy
			Direct	Indirect	ΔE (eV)
1	BaBSm0	399	3.4	3.22	0.18
2	BaBSm0.5	280	4.4	4.35	0.05

Luminescence (PLE and PL studies of BaBSm0.5 glass) analysis

In order to analyze luminescence properties of the SbBSm0.5 glass, it is essential to know the suitable excitation wavelengths of Sm^{3+} ions. 600nm wavelength monitored PL excitation spectrum of the BaBSm0.5 glass is measured using Xenon as excitation source at room temperature is as shown in Figure 4. From the figure several bands were observed in the visible region at 345, 361, 375, 402, 417, 438, 470, 511, 535 and 545nm. All these are identified due to 4f – 4f inner shell transitions of Sm^{3+} ions. Among these 402nm peak is strongest one with high intensity and the transitions were assigned from $^6H_{5/2} \rightarrow {}^4D_{5/2}$, $^4D_{3/2}$, $^4D_{1/2}$, $^6P_{3/2}$, $^6P_{5/2,}$ $^4G_{9/2}$, $^4I_{9/2} + {}^4M_{15/2} + {}^4I_{7/2}$, $^4F_{3/2}$ respectively.

The emission spectrum of BaBSm0.5 glass has been recorded at room temperature with the excitation wavelength 402nm and it is shown in figure 5.. From the emission spectrum four bands are observed at 563, 600, 647nm and 712nm. Among these 600 and 647 nm are having high intensity along with hump at 712nm with low intensity is observed in the visible region. These emission bands are the characteristic emissions of Sm^{3+} ion and were assigned from $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (yellow), $^6H_{7/2}$ (orange), $^6H_{9/2}$ (red) and $^6H_{11/2}$ (deep red) respectively. The emission intensities of orange and red were almost equal, where as the deep red emission intensity is negligible when compared to orange red emission. Finally the glass emits red colour which we can see in the CIE diagram shown in the section 3.4 and also shown in the inset in the figure 5. The energy level diagram of excitation and emission transitions is shown in the figure 8.

Figure 6 is the PL emission spectrum of the BaBSm0.5 glass measured at 280nm as excitation source at room temperature. The PL emission spectrum was measured range from 250 – 650 nm wavelengths to know the emissions were useful for display applications. It exhibits emission peaks at 469, 562 nm in the visible region. It is concluded that under 280nm excitation wavelength the glass emits yellow colour which is useful for display applications.

Figure 7 is the PL emission spectrum of the BaBSm0.5 glass measured at 460nm as excitation source at room temperature. The PL emission spectrum was measured range from 560nm to 700nm wavelength to know the emissions were useful for LED applications. It exhibit emission peaks at 563, 600, 626 and 647nm in the visible region and among these emissions 600nm peak has highest intensity. It is concluded that under 460nm excitation the glass emits red colour which is useful for LED applications.

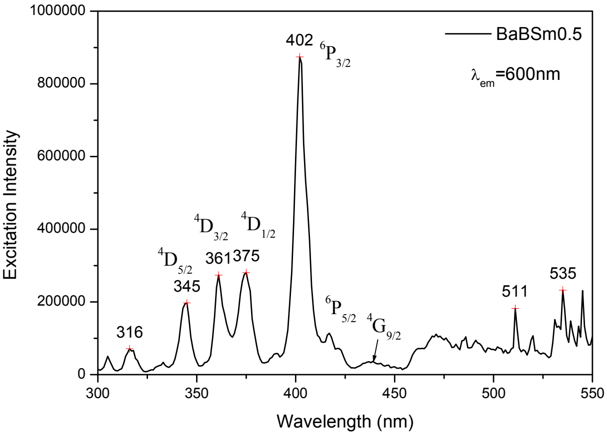

Figure 4 Excitation spectrum of Ba BSm0.5 glasses monitored at 600nm wavelength

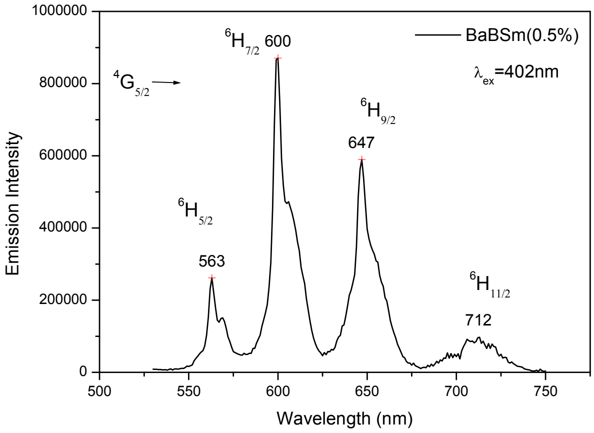

Figure 5 Emission spectrum of BaBSm0.5 glass at 402nm excitation wavelength

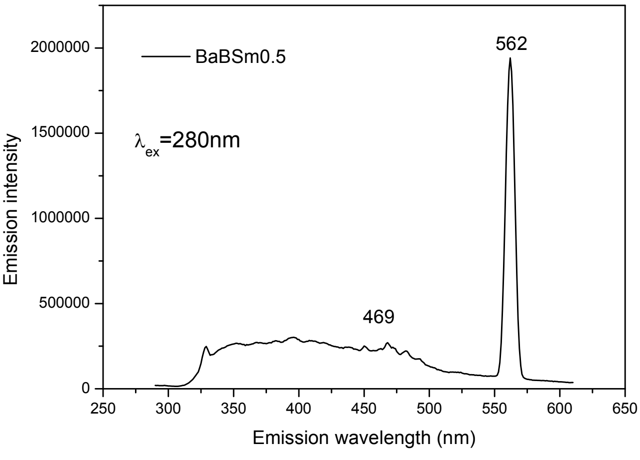

Figure 6 Emission spectrum of BaBSm0.5 glass at 280nm excitation wavelength

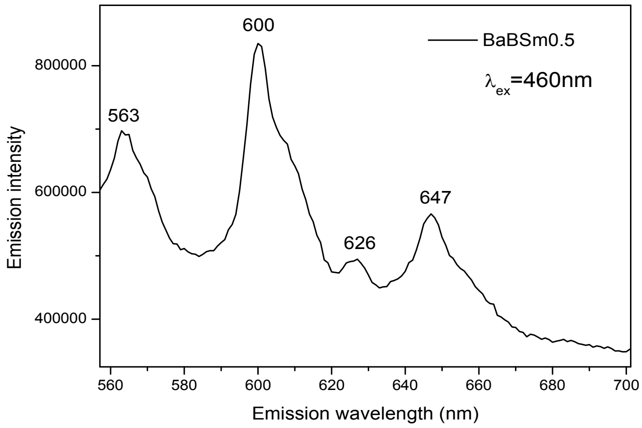

Figure 7 Emission spectrum of BaBSm0.5 glass at 460nm excitation wavelength

The luminescence behaviour of Sm^{3+} doped barium borate glass has been studied throughout the emission spectral measurement. The luminescence spectra have been recorded by monitoring an excitation at 280 nm as shown in Fig. 6. The spectra contain luminescence bands in the blue broad band region at 478 nm ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), greenish-yellow sharp band region at 562 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) are observed [13].

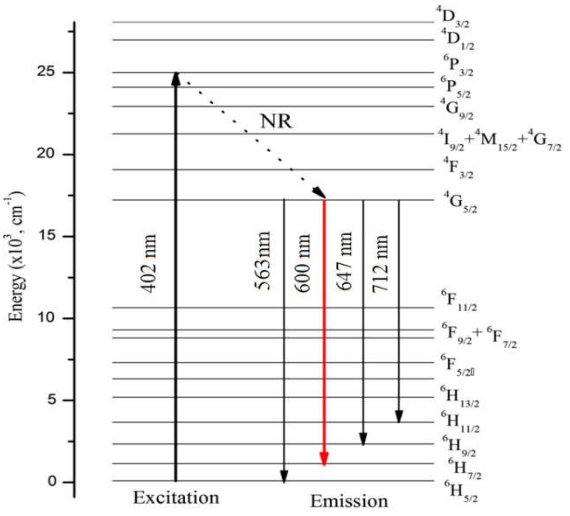

Figure 8 Energy level diagram of excitation and emission transitions of BaBSm0.5 glass

Commission Internationale de l'Elcairage (CIE) study

The luminescent intensity of the emission spectral measurements has been characterized using the CIE 1931 chromaticity diagram. Fig. 9 shows the CIE chromaticity diagram for the prepared glass (λ_{ex} =402 nm) and the values of the (x, y) color coordinates are found to be (0.613, 0.387) corresponding to the prepared SbBSm0.5. From the CIE plot it is observed that prepared glass sample emit orange red light under the excitation of 402 nm. Such glass can be applicable for red LED.

The color temperature of a light source is that the temperature of the planckian's black body radiator, whose radiation is the same chromaticity as the light source. The chromaticity of nature and artificial light sources, including day light are not on this locus, hence "correlated color temperature" (CCT) is used to indicate the temperature of the black body whose colour property is nearest to that of the light source. Generally white light deals with CCT from the planckian locus approximation, the range of CCT can be derived from CIE coordinates using the third power polynomial which is applied between 2222 K and 13,000 K. The CCT of glass BaBSm is undefined. It is concluded that this glass can be useful for the preparation of red LED with highest emission intensity. The CIE diagrams were drawn using Radiant Imaging software version 2.0.

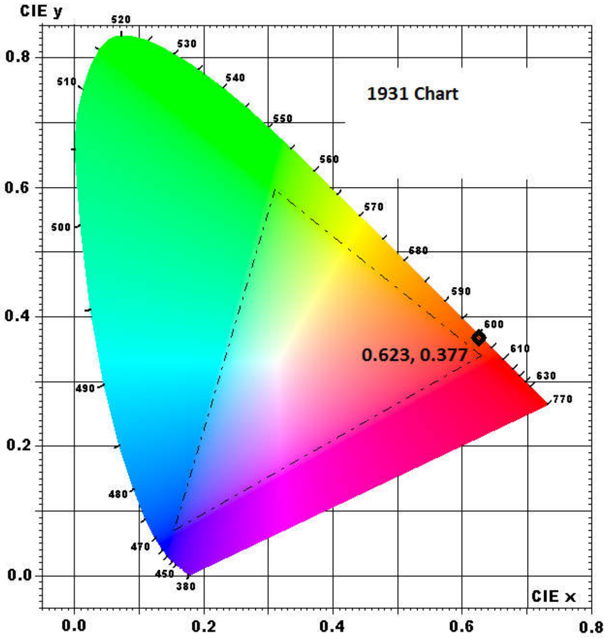

Figure 9 CIE Co-ordinates of Sm doped BaB glass depicted on 1931 chart

CONCLUSIONS

The BaBSm0.5 and pure BaBSm0 glasses were prepared and characterized for their optical and luminescence properties using melt quenching technique successfully.

From the value of Urbach energy, it is observed that the BaBSm0.5 glass has low value of structural disorder, which indicates the strong structural stability.

The absorption spectra consist of from $^6H_{5/2}\rightarrow{}^4I_{11/2}$, $^6P_{5/2}$, $^6P_{3/2}$, $^6P_{7/2}$ and $^4D_{3/2}$ were observed at wavelengths 486 nm, 402 nm, 375 nm, 360 nm and 343 nm respectively.

The excitation spectrum consists of several bands were observed in the visible region at 345, 361, 375, 402, 417, 438, 470, 511, 535 and 545nm. All these are identified due to 4f – 4f inner shell transitions of Sm^{3+} ions. Among these 402nm peak is strongest one with high intensity and the transitions were assigned from $^6H_{5/2}\rightarrow{}^4D_{5/2}$, $^4D_{3/2}$, $^4D_{1/2}$, $^6P_{3/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4I_{13/2}$ respectively.

The emission spectrum of BaBSm0.5 glass measured at 402nm excitation wavelength. From the figure three emission bands at 563, 600, 647nm with high intensity along with one hump at 712nm with low intensity is observed in the visible region. These emission bands are the characteristic emissions of Sm^{3+} ion and were assigned from $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (yellow), $^6H_{7/2}$ (orange), $^6H_{9/2}$ (red) and $^6H_{11/2}$ (deep red) respectively which can be useful for LED applications.

The emission band at 478 and 562nm were observed under 280nm excitation wavelength, the yellow band is sharp with double intensity than the blue band intensity which can be useful for display applications.

The BaB glass doped with 0.5 mol% of Sm_2O_3 gives the good result for luminescence properties.

On comparing the observed results of our Sm^{3+} doped BaB simple glass matrix with other Sm^{3+} doped complex glass matrix, it is concluded that the transitions takes place between dopant (Sm) ion and Boron ion in B_2O_3.

References

1. Arunakumar S, Venkataiah G, Marimuthu K, Spectrochim. Acta, Part A: Molecular and Biomolecular spectroscopy 136 (2015) 1684-1697
2. Sreedhar V B, Ramachari D, Jayasankar C K, Physica B 408 (2013) 158-163.
3. Sunil Thomas, Nayab Rasool Sk, Rathaiah M, Venkatramu V, Cyriac Joseph, Unnikrishnan N V, Journal of Non-Crystalline Solids 376 (2013) 106-116.
4. Manoj Kumar G, Shivakiran Bhaktha B N, Narayana Rao D, Optical Materials 28 (2006) 1266-127
5. LI H., Wang C., YU H., Liang X., Yang S., Spectrosc. Lett., (2014)
6. Kummara Venkata Krishnaiah, Kagola Upendra Kumar, Chalicheemalapalli Kulala Jayasankar, Mater. Express, 3 (2013) 61-70
7. A. Mierzejewski, S.A. Saunders, H.A.A. Sidek, B. Bridg, J. Non-Cryst. Solids 104
8. (1988) 323.
9. K. Hairao, S. Todoroki, D.H. Cho, N. Soga, Opt. Lett. 18 (1993) 1586.
10. A. Kurita, T. Kushida, T. Izumitani, M. Matsukawa, Opt. Lett. 19 (1994) 314–316.
11. A. Patra, D. Kundu, D. Gunguli, Mater. Lett. 32 (1997) 43.
12. I.Z. Hager, R. El-Mallawany, A. Bulon, Physica B 406 (2011) 972–980.
13. B. Eariah, G. Sudha, G. Bhat, J. Phys. Chem. Solids 68 (2007) 581–587.
14. C. Venkateswarlu, M. Seshadri, Y.C. Ratnakaram, Opt. Mater. 33 (2011) 799–805.
15. I. Arul rayappan, K. Selvaraju, K. Marimuthu, Physica B 406 (2011) 548–555.
16. S. Rai, L. Bokatial, P.J. Dihingia, J. Lumin. 131 (2011) 978–983.
17. W.T.Carnall, P.R.Fields, J.Morrison and R.Sarup, J.Chem. Phys, 52 (1970), 4054
18. C.K.Jayasankar and P.Babu, J.Alloy and Comp. 307 (2000), 82

How to cite this article:

Ch.Vijay Anil Dai *et al.*, 2019, Optical and Luminescence Properties of sm3+ (0.5%) Doped Bao-b2o3 Glass. *Int J Recent Sci Res.* 10(06), pp. 33051-33056. DOI: http://dx.doi.org/10.24327/ijrsr.2019.1006.3595

****