

## Influence of alkaline earth modifiers on luminescence characteristics of Dy<sup>3+</sup> ions in lead zinc antimonate glasses

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**ABSTRACT:** Sb<sub>2</sub>O<sub>3</sub>-PbO -ZnO: Dy<sub>2</sub>O<sub>3</sub> glasses mixed with three different modifier oxides viz., BaO, CaO and SrO were prepared. The influence of modifier oxide on the luminescence characteristics of Dy<sup>3+</sup> ions has been investigated. Using the intensities of various absorption bands of Dy<sup>3+</sup> ions, the Judd-Ofelt parameters  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$  have been evaluate and tabulated. Together with the J-O parameters and the luminescence spectra, the evaluated various radiative properties like transition probability A, Total radiative probability A<sub>T</sub>, branching ratio  $\beta_r$ , the radiative life time  $\tau_r$ , and the emission cross-section  $\sigma^E$  for various emission levels of Dy<sup>3+</sup> ions have been evaluated and reported. The values of these parameters were found to be influenced by modifier oxides. Among the three modifier oxides mixed glasses, the glasses mixed with BaO mixed glasses exhibited the highest luminescence efficiency. The quantitative analysis of results were analyzed in the light of structural modifications taking place in the glass network with the help of IR spectral studies.

**Key words:** Sb<sub>2</sub>O<sub>3</sub>-PbO -ZnO Dy<sub>2</sub>O<sub>3</sub>: Dy<sup>3+</sup> glasses; Modifier oxides; luminescence efficiency, J-O parameters and life time

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### I. INTRODUCTION

The rare earth ions of dysprosium (Dy<sup>3+</sup>) mixed glasses and phosphors are being extensively used as white light luminescent materials. These ions are well known and is interesting for ions for studying fluorescence properties due to their prominent emission transitions viz., <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> (forced electric dipole transition) in the blue region and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> (magnetic dipole transition) in the yellow region. The ratio of intensities of these two emissions viz., (Y/B) of Dy<sup>3+</sup> ion differs from material to material and plays a crucial role in the white light emission of this ion. Additionally, dysprosium ions also exhibit bands in the NIR region at about 3.02 μm (due to <sup>6</sup>H<sub>13/2</sub> → <sup>6</sup>H<sub>15/2</sub> transition) and at 1.34 μm (due to <sup>6</sup>H<sub>11/2</sub> → <sup>6</sup>H<sub>13/2</sub> transition) that are useful for fiber amplifiers [1-5].

Among several glass hosts, the non-conventional antimony oxide (Sb<sub>2</sub>O<sub>3</sub>) based glasses (a heavy metal oxide class of glasses) are predicted to be highly suitable for hosting such longer wavelength emission lasing ions. These glasses possess high density, high refractive index, high dielectric constant (when compared with conventional borate and phosphate glasses), good photothermal properties and

exhibit exceptionally good infrared transmission with low phonon losses [6, 7]. However, Sb<sub>2</sub>O<sub>3</sub> is an incipient glass former and as such does not readily form the glass. Hence, the addition of modifier oxides like PbO is necessary to Sb<sub>2</sub>O<sub>3</sub> for achieving a good glass. Such addition enhances the density and the refractive index of the material and also minimizes the phonon losses. Further, Sb<sub>2</sub>O<sub>3</sub> glasses do exhibit non-linear optical properties. In fact several studies on non-linear optical (NLO) properties of these heavy metal oxide glasses were reported earlier and the non-linear optical effects were attributed to the displacement of 5s<sup>2</sup> lone pair of electrons in the trigonal bipyramidal structure of Sb<sub>2</sub>O<sub>3</sub>. Earlier, we have also carried out a considerable number of studies on NLO properties of these glasses and glass ceramics using optical poling technique and obtained NLO effects were attributed to such displacement [8, 9].

When lead antimony zinc glasses doped with rare-earth ions are added with different modifier oxides, the structural modifications and local electrostatic field variations near the dopant rare earth ion take place. The addition of BaO is a well-known modifier and may enter the glass network by

transforming two Q3 tetrahedra polyhedron is formed (as mentioned earlier) when it is surrounded by such two Q2 and several Q3 tetrahedrons. The addition of CaO, can form one CaO<sub>n</sub> polyhedron is formed by the Ca<sup>2+</sup> ions. The new substructure behaves as a defect in the host glass network. Though the effect of the new substructure on the remaining network is smaller, the influence of the remaining network on the environment of the calcium cation is very strong. Higher the concentration of CaO, the stronger is the degree of disorder in glass network. The degree of depolymerization of the glass network is however strongly dependent on the ionic radius of the modifier ion and its compatibility with the network forming ions in the glass network. Overall, the variation of modifier oxide changes the symmetry and (or) covalency of the glass network at the rare earth ion; as a result there will be strong variations on luminescence efficiency of the dopant rare earth ion in the host glass network. Another, alkaline earth ion like SrO, It may be noted here even though the ionic radius of Sr<sup>2+</sup> ion (1.02 Å) is greater than Ca<sup>2+</sup> and Ba<sup>2+</sup> ions, its ionic radius is closer to that of Dy<sup>3+</sup> ions (1.03 Å).

Among various rare earth ions, Dy<sup>3+</sup> ions are known due to their prominent emission in the blue and yellow regions. The antimony lead zinc glasses possess all the requisite conditions to host such an interesting rare earth ion. Additionally, by varying the modifiers in the glass network there will be a strong variation on intensity ratio of Y/B of Dy<sup>3+</sup> ion which plays a crucial role in the white light emission of this ion. The objective of the present investigation is to characterize the optical absorption and the fluorescence spectra of Dy<sup>3+</sup> ions in Sb<sub>2</sub>O<sub>3</sub>-PbO - ZnO glasses mixed with three interesting alkaline earth modifier oxides, viz. BaO, CaO and SrO and to throw some light on the relationship between the structural modifications in the glass network and luminescence efficiency.

## II. EXPERIMENTAL

The details of chemical composition of the samples used the study are as follows:

SrSbZDy: 59Sb<sub>2</sub>O<sub>3</sub>—10 PbO— 20ZnO — 10SrO —Dy<sub>2</sub>O<sub>3</sub>

CaSbZDy:59Sb<sub>2</sub>O<sub>3</sub>—10PbO—20ZnO—10CaO—1Dy<sub>2</sub>O<sub>3</sub>

BaSbZDy:59Sb<sub>2</sub>O<sub>3</sub>—10PbO—20ZnO—10BaO—1Dy<sub>2</sub>O<sub>3</sub>

The glasses were prepared by suitable chemical compounds viz.,PbO,Sb<sub>2</sub>O<sub>3</sub>, CaO, SrO,BaOand Dy<sub>2</sub>O<sub>3</sub> powders (99.99 % pure) were thoroughly mixed in an agate mortar and melted in

silica crucibles in the temperature range 1400–1450 °C in a PID temperature–controlled furnace for about 30 min. until bubble-free transparent liquid was formed, then the resultant melt liquid was poured in a brass mould and subsequently annealed at 350 °C. The synthesized lead antimonate glasses (free from traditional glass forming oxides) are found to be perfect transparent. The amorphous nature of the samples was confirmed by X–ray diffraction. Finally, the samples were polished to obtain smooth, transparent and uniform surface slabs for optical measurements to the average dimensions of 1.0 cm x 1.0 cm x 0.2 cm. The density was measured by Archimedes' principle using o-xylene as the buoyant liquid.

The refractive index, n, is measured on Abbe refractometer using sodium wavelength (589.3nm) using 1-bromonaphthalene as a contact liquid. The optical absorption spectra were obtained by using the JASCO UV-vis-NIR spectrophotometer in the wavelength range 200 – 1800 nm for Dy<sup>3+</sup> ions, respectively. Fluorescence spectra were recorded at room temperature using Thermo Scientific (Lumina) Luminescence spectrophotometer in the wavelength region 200–900 nm. Infrared transmission spectra were recorded at room temperature by using Shimadzu IR Affinity-1S spectrophotometer with resolution of 4 cm<sup>-1</sup> in the wavelength range 400—2000 cm<sup>-1</sup>.

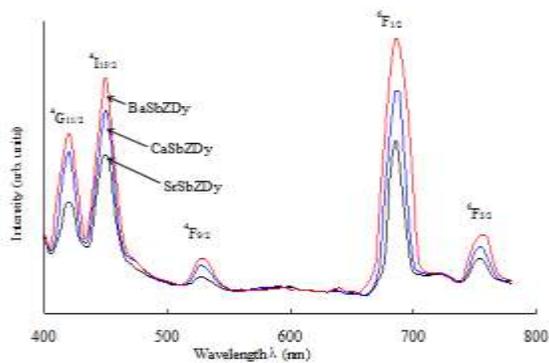
## III. RESULTS AND DISCUSSION

From the measured values of samples are exhibits average density d and molecular weight  $\bar{M}_0$  of Sb<sub>2</sub>O<sub>3</sub>-PbO -ZnO-MO (M= Ba, Ca, & Sr): Dy<sub>2</sub>O<sub>3</sub> glasses, various other physical parameters such as Dy<sup>3+</sup> ion concentration N<sub>i</sub>, Dy<sup>3+</sup> ion separation r<sub>i</sub>, in Sb<sub>2</sub>O<sub>3</sub>-PbO -ZnO-MO (M = Ba, Ca, & Sr): Dy<sub>2</sub>O<sub>3</sub> glass samples are computed using the conventional formulae and are presented in Table 1.

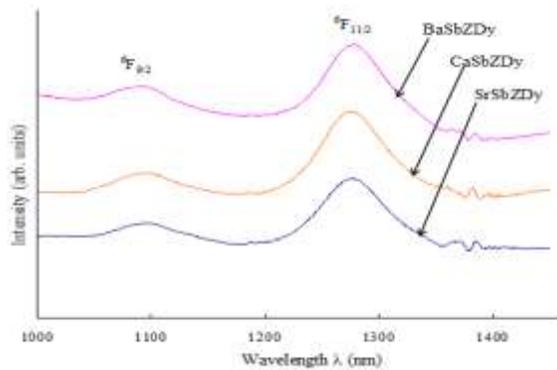
**Table 1** Physical parameters of Sb<sub>2</sub>O<sub>3</sub>-PbO-ZnO-MO (CaO, SrO & BaO):Dy<sub>2</sub>O<sub>3</sub> glasses.

| Glass   | Avg. Mol. Wt. M | Density d (g/cm <sup>3</sup> ) | Dy <sup>3+</sup> ion con. N <sub>i</sub> (10 <sup>20</sup> cm <sup>-3</sup> ) | Inter ionic distance of Dy <sup>3+</sup> ions r <sub>i</sub> (nm) | Polaron radius R <sub>p</sub> (nm) | Field Strength E <sub>f</sub> (x10 <sup>17</sup> cm <sup>-2</sup> ) | Refractive index, n |
|---------|-----------------|--------------------------------|---|---|------------------------------------|---|---------------------|
| SrSbZDy | 281.95          | 5.228                          | 11.157  | 2.077   | 1.259                              | 1.091   | 1.642               |
| CaSbZDy | 277.44          | 5.963                          | 13.183  | 1.965   | 1.331                              | 1.091   | 1.665               |
| BaSbZDy | 291.90          | 6.314                          | 12.717  | 0.922   | 2.534                              | 0.373   | 1.685               |

The optical absorption spectra(Figs. 1 (a) and 1 (b))of Dy<sup>3+</sup> ion doped Sb<sub>2</sub>O<sub>3</sub>-PbO -ZnO-MO glasses recorded at room temperature in the wavelength range 200–2000 nm, exhibited the following absorption bands, all from the ground state <sup>6</sup>H<sub>15/2</sub>.  
<sup>6</sup>H<sub>15/2</sub> → <sup>4</sup>G<sub>11/2</sub> + <sup>4</sup>M<sub>21/2</sub>, <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub>, <sup>6</sup>F<sub>1/2</sub>, <sup>6</sup>F<sub>3/2</sub> (UV, visible region) and <sup>6</sup>F<sub>9/2</sub>, <sup>6</sup>F<sub>11/2</sub>+ <sup>6</sup>H<sub>9/2</sub> (NIR region)



**Fig.1 (a)** Optical absorption spectra of Sb<sub>2</sub>O<sub>3</sub>-PbO -ZnO-MO (M= Ba, Ca, & Sr): Dy<sub>2</sub>O<sub>3</sub> glasses recorded in the visible region.



**Fig. 1(b)** Optical absorption spectra of Sb<sub>2</sub>O<sub>3</sub>-PbO ZnO-MO (M= Ba, Ca, & Sr): Dy<sub>2</sub>O<sub>3</sub> glasses recorded in the NIR region.

Among these, the absorption band due to <sup>6</sup>H<sub>15/2</sub> → <sup>6</sup>F<sub>1/2</sub> transition is observed to be predominant in the spectra of all the three glasses. The pattern of the absorption bands for the three different modifier oxide mixed glasses remains the same; however, the area under the given peak is observed to vary with the change in modifier oxide. The comparison of three spectra indicated the highest intensity of all the bands in the spectrum of BaO mixed glasses when compared with that of other two glasses.

The oscillator strengths (OS) of the electric dipole transition between two states have been calculated using the standard Judd-Ofelt (JO) theory, with the conventional equation [10, 11],

$$f_{cal} = \frac{8\pi^2 mc v \chi}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle f^N [\gamma, S, L]J || U^{\lambda} || f^N [\gamma', S', L']J' \rangle (1)$$

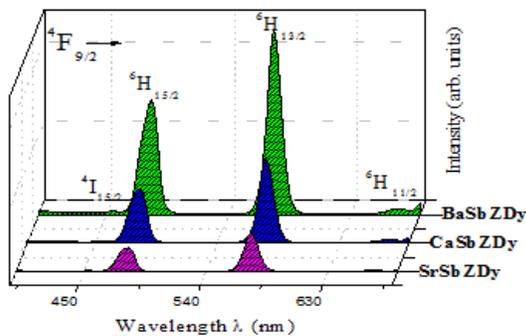
where m is the electron mass, c the speed of light, h is the Planck's constant,  $\chi = \frac{(n^2+2)^2}{9n}$  the local field correction, n is the refractive index, and the bra- and ket-vectors  $\langle f^N [\gamma, S, L]J || U^{\lambda} || f^N [\gamma', S', L']J' \rangle$  stands for the initial and final states, respectively, with all necessary sets of quantum numbers in square brackets.  $||U^{\lambda}||$  are the reduced matrix elements of the unit tensor operators. The  $||U^{\lambda}||$  reduced matrix elements have been additionally evaluated, using recent reference data for the Dy<sup>3+</sup> Hamiltonian parameters [12].

The Judd-Ofelt intensity parameters of  $\Omega_{\lambda}(\lambda = 2, 4 \text{ and } 6)$  for the three glasses (BaDy, CaDy and SrDy) exhibited acceptable fitting between theoretical and experimental values. The J-O parameters, viz.,  $\Omega_{\lambda}$  are found to be in the order of  $\Omega_2 > \Omega_6 > \Omega_4$  for all the three glasses (Table 2). Out of the three J-O parameters the value of  $\Omega_2$  is mainly connected with the covalence and structural changes in the vicinity of Dy<sup>3+</sup> ions (connected with the short-range effect), whereas the other two parameters viz.,  $\Omega_4$  and  $\Omega_6$  are strongly dependent on the vibrational levels of various structural units in the glass network. The comparison of  $\Omega_2$  parameter for Dy<sup>3+</sup> ions indicates (Table 2) the lowest value for BaO mixed glasses and the highest for SrO mixed glasses. This observation indicates the highest covalent nature for the SrO mixed glasses.

**Table 2** The absorption band energies and the oscillator strengths for the transitions of Dy<sup>3+</sup> ions in Sb<sub>2</sub>O<sub>3</sub>-PbO-ZnO-MO (CaO, SrO & BaO) glass system.

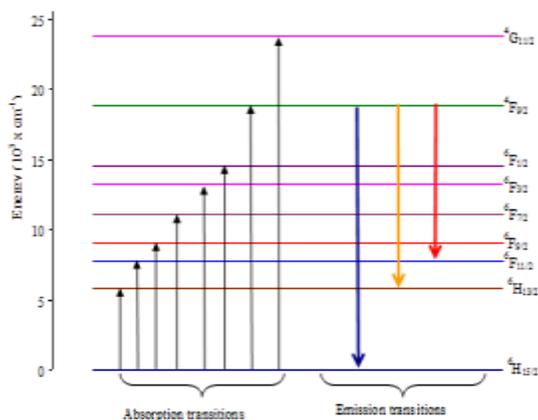
| Glass   | BaOZDy          |                               |                               | CaOZDy          |                               |                               | SrOZDy          |                               |                               |
|---|-----------------|-------------------------------|-------------------------------|-----------------|-------------------------------|-------------------------------|-----------------|-------------------------------|-------------------------------|
|   | Transition (nm) | $\Omega_2$ (10 <sup>3</sup> ) | $\Omega_4$ (10 <sup>3</sup> ) | Transition (nm) | $\Omega_2$ (10 <sup>3</sup> ) | $\Omega_4$ (10 <sup>3</sup> ) | Transition (nm) | $\Omega_2$ (10 <sup>3</sup> ) | $\Omega_4$ (10 <sup>3</sup> ) |
| <sup>6</sup> F <sub>1/2</sub>   | 700             | 0.624                         | 0.384                         | 706             | 0.421                         | 0.386                         | 711             | 0.336                         | 0.387                         |
| <sup>6</sup> F <sub>3/2</sub>   | 924             | 0.228                         | 0.263                         | 927             | 0.128                         | 0.303                         | 932             | 0.221                         | 0.392                         |
| <sup>6</sup> F <sub>9/2</sub>   | 1226            | 0.372                         | 0.225                         | 1228            | 0.262                         | 0.222                         | 1232            | 0.221                         | 0.116                         |
| <sup>6</sup> F <sub>11/2</sub>  | 1458            | 1.518                         | 1.328                         | 1456            | 1.423                         | 1.383                         | 1477            | 0.921                         | 0.326                         |
| <sup>6</sup> F <sub>15/2</sub>  | 1898            | 0.112                         | 0.139                         | 1898            | 0.168                         | 0.176                         | 1899            | 0.172                         | 0.060                         |
| <sup>6</sup> F <sub>9/2</sub>   | 2282            | 1.106                         | 0.872                         | 2227            | 0.883                         | 0.736                         | 2222            | 0.646                         | 0.427                         |
| <sup>6</sup> F <sub>11/2</sub> - <sup>6</sup> F <sub>9/2</sub> (no division 10 <sup>3</sup> ) | 2578            | 0.712                         | 0.587                         | 2576            | 0.603                         | 0.591                         | 2589            | 0.474                         | 0.221                         |
| $\Omega_2$ (10 <sup>3</sup> cm <sup>2</sup> )   |                 | 0.324                         |                               |                 | 0.519                         |                               |                 | 0.548                         |                               |
| J-O Parameters  | $\Omega_2$      | $\Omega_4$                    | $\Omega_6$                    | $\Omega_2$      | $\Omega_4$                    | $\Omega_6$                    | $\Omega_2$      | $\Omega_4$                    | $\Omega_6$                    |
| $\Omega_2$ (10 <sup>3</sup> cm <sup>2</sup> )   | 1.41            | 0.21                          | 0.36                          | 2.24            | 0.37                          | 0.82                          | 2.35            | 0.36                          | 0.66                          |

Excitation and emission spectra of the titled glasses recorded at room temperature are presented in (Fig. 2) the excitation spectra (monitored at 574 nm) exhibited an intense band at wavelength of 348 nm and the same was used for recording photoluminescence (PL) spectra. The PL spectra of all the glasses exhibited the following emission bands originated from  $^4F_{9/2}$  excited level:  
 $^4F_{9/2} \rightarrow ^4I_{9/2}$ ,  $^6H_{15/2}$ ,  $^6H_{13/2}$ ,  $^6H_{11/2}$



**Fig.2** Emission ( $\lambda_{exc} = 348 \text{ nm}$ ) spectra of  $\text{Dy}^{3+}$  doped  $\text{Sb}_2\text{O}_3\text{-PbO-ZnO-MO}$  (CaO,SrO & BaO ) glasses.

Out of these,  $^4F_{9/2} \rightarrow ^6H_{13/2}$ , yellow emission transition (with  $\square L=2$ ,  $\square J=2$ ), is observed to be hypersensitive. The intensity of all the emission bands is observed to be the highest in the spectrum of BaO mixed glasses among the three glasses studied. The energy level diagram consisting of various absorption and emission transitions of  $\text{Dy}^{3+}$  ions for the glass modifier BaD sample is presented in Fig. 3.



**Fig.3** Energy level diagram representing absorption and emission processes in  $\text{Dy}^{3+}$  doped  $\text{Sb}_2\text{O}_3\text{-PbO-ZnO-MO}$  (CaO,SrO & BaO ) glass system.

The radiative parameters viz., spontaneous emission probability,  $A_r$ , the total emission

probability,  $A_T$ , the radiative lifetime,  $\tau_r$  and the fluorescent branching ratio  $\beta_r$  of different transitions originated from  $^4F_{9/2}$  level of  $\text{Dy}^{3+}$  ions have been evaluated using the standard relations and presented in Table 3. The emission cross-section  $\sigma(\lambda)$  is evaluated using

$$\sigma(\lambda) = \frac{\lambda^4 A_{J'J''}}{8\pi n^2 c \Delta\lambda_{eff}} \quad (3)$$

and are furnished in Table 3. In Eq. (3),  $\lambda$  is the emission peak wavelength and  $\Delta\lambda_{eff}$  is its effective line width,  $c$  is the velocity of light and  $n$  is the refractive index. The value of  $\beta_r$  is found to be the highest for BaO mixed glasses when compared with that of other two glasses.

**Table 3** Various radiative properties of transitions of  $\text{Dy}^{3+}$  ions in  $\text{Sb}_2\text{O}_3\text{-PbO-ZnO-MO}$  (CaO,SrO & BaO ) glasses.

| Transition                             | BaO                                     |         | CaO                                     |         | SrO                                     |         |
|--|---|---------|---|---------|---|---------|
|  | Intensity (a.u.)                        | Y/B (%) | Intensity (a.u.)                        | Y/B (%) | Intensity (a.u.)                        | Y/B (%) |
| $^4F_{9/2} \rightarrow ^6H_{13/2}$     | 2860                                    | 22.5    | 2860                                    | 22.5    | 1211                                    | 10.0    |
| $^4F_{9/2} \rightarrow ^6H_{15/2}$     | 1743                                    | 13.7    | 1743                                    | 13.7    | 1011                                    | 8.5     |
| $^4F_{9/2} \rightarrow ^6H_{11/2}$     | 1517                                    | 11.9    | 1517                                    | 11.9    | 1106                                    | 9.5     |
|  | $A_r = 1.79 \times 10^4 \text{ s}^{-1}$ |         | $A_r = 1.79 \times 10^4 \text{ s}^{-1}$ |         | $A_r = 1.79 \times 10^4 \text{ s}^{-1}$ |         |
|  | $\tau_r = 4.57 \text{ ns}$              |         | $\tau_r = 4.57 \text{ ns}$              |         | $\tau_r = 4.57 \text{ ns}$              |         |
| $\sigma_{475} (10^{-20} \text{ cm}^2)$ | 1.13                                    |         | 1.13                                    |         | 1.13                                    |         |
|  | 1.07                                    |         | 1.07                                    |         | 1.07                                    |         |
|  | 1.07                                    |         | 1.07                                    |         | 1.07                                    |         |

Among the three intense bands in the emission spectra,  $^4F_{9/2} \rightarrow ^6H_{13/2}$  (yellow), magnetic dipole transition (MD), exhibited the highest intensity, whereas  $^4F_{9/2} \rightarrow ^6H_{15/2}$  (blue) due to electric dipole transition (ED) exhibited comparatively lower intensity. The ratio of intensities of MD and ED bands is a measure of the symmetry of the local environment of trivalent of 4f ions. From the emission spectrum Y (I  $^4F_{9/2} \rightarrow ^6H_{13/2}$ ) / B (I  $^4F_{9/2} \rightarrow ^6H_{15/2}$ ) integrated ratio exhibited the maximum value for CaO mixed glasses and the lowest for SrO mixed glasses. The higher value of Y/B ratio indicates the larger concentration of dissociated  $\text{Dy}^{3+}$  ions from Dy-O-Dy bonds in the glass [13]. Among the three modifier ions, the ionic radius of  $\text{Ba}^{2+}$  ion is larger when compared to that of  $\text{Sr}^{2+}$  ion. As a result, there is a possibility for higher degree of de-polymerization of the glass network. Such tendency leads to the observed higher value of Y/B for this glass.

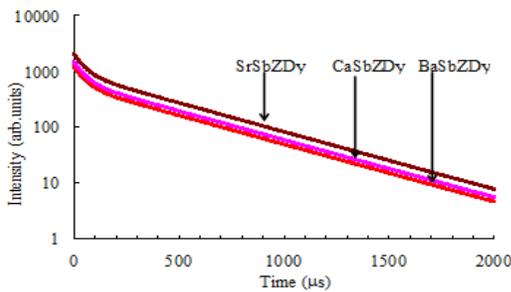
| Glass | Measured<br>(□ sec)<br>(□ <sub>mes</sub> ) | Calculated<br>(□□sec)<br>(□ <sub>R</sub> ) | Quantum<br>efficiency<br>(□□□□) |
|-------|--|--|---------------------------------|
| BaD   | 419  | 571  | 73.38                           |
| CaD   | 376  | 532  | 70.67                           |
| SrD   | 325  | 518  | 62.74                           |

**Table 4.** Summary of the data on life time measurements of <sup>4</sup>F<sub>9/2</sub> excited level (λ<sub>exc</sub>= 348 nm) and (λ<sub>emi</sub> = 574 nm) .

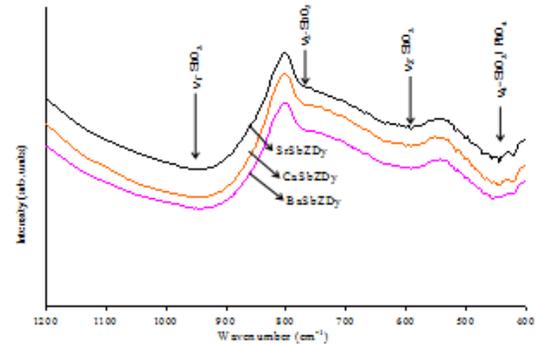
We have recorded the decay curves of the <sup>4</sup>F<sub>9/2</sub> excited level of Dy<sup>3+</sup> ions for all the three glasses and presented in Fig. 4.

The life times (□<sub>mes</sub>) evaluated from slow decay part of these curves are presented in Table 4. The value of □<sub>mes</sub> is observed to be in the following order: SrD<CaD<BaD. The lower radiative life time of SrDy samples indicates more covalent environment around the Dy<sup>3+</sup> ions in the glass network and it indicates the presence of higher vibrational frequencies. Relatively, lower decay time of SrO mixed glasses suggests that the emission is from clustered Dy<sup>3+</sup> ions. The quantum efficiency (□□□□<sub>mes</sub>□<sub>R</sub>, defined as the radiative portion of the total relaxation rate of a given energy level is found to be the highest for BaO mixed glasses.

**Fig.4** Decay curves of Dy<sup>3+</sup> doped Sb<sub>2</sub>O<sub>3</sub>-PbO-ZnO-MO (CaO,SrO & BaO) glasses recorded at room temperature.



The infrared transmission spectrum of MO (M=Ba, Ca & Sr)-ZnO-PbO-Sb<sub>2</sub>O<sub>3</sub>:Dy<sup>3+</sup> doped glasses presented in Fig.5. The spectra of all the glasses exhibited conventional bands due to the ν<sub>1</sub> (symmetrical stretching) and ν<sub>2</sub> (bending vibrations) of SbO<sub>3</sub> structural groups at about 950 cm<sup>-1</sup> and 600 cm<sup>-1</sup>, respectively. The spectra also exhibited weak double degenerate stretching (ν<sub>3</sub>) and bending (ν<sub>4</sub>) vibrational bands of SbO<sub>3</sub> structural units at about 770 and 458 cm<sup>-1</sup>, respectively [14–16]. This region may also consist of the band due to the vibrations of ZnO<sub>4</sub> structural units

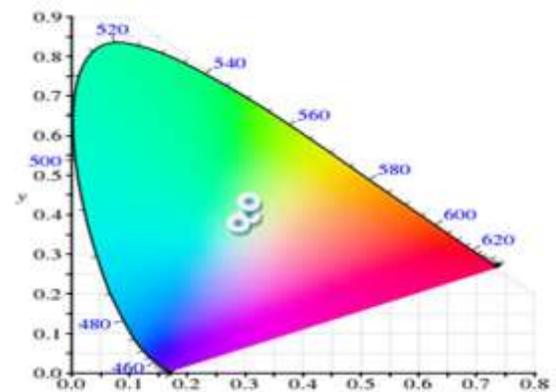


**Fig 5.** IR spectra of Sb<sub>2</sub>O<sub>3</sub>-PbO-ZnO-MO (CaO,SrO & BaO): Dy<sub>2</sub>O<sub>3</sub> glass system.

The intensity of bands due to asymmetrical vibrations is found to be the highest for BaO mixed glasses. This observation also supports the view point that there is a higher degree of de-polymerization of the glass in BaO mixed glasses. It may be noted here even though the ionic radius of Sr<sup>2+</sup> ion (1.02 Å) is greater than Ca<sup>2+</sup> and Ba<sup>2+</sup> ions, its ionic radius is closer to that of Dy<sup>3+</sup> ions (1.03

Å). Hence there is a possibility for cross linking of these ions with Dy<sup>3+</sup> ions. As a result there will be more phonon losses hence there is a decrease in the luminescence efficiency of these glasses.

The chromaticity coordinate values of the studies were evaluated from the PL studies using the Commission International de l'Eclairage (CIE) system. In Fig.6, the CIE plot with color coordinates of the three glasses evaluated from the PL spectra is presented. The CIE color coordinates for Dy<sup>3+</sup> ions were found to be shifted towards slightly yellow region for BaO mixed glasses when compared with the other two glasses.



**Fig. 6** CIE plot. represents color corresponding to the light emitted due to <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>13/2</sub> transition of Dy<sup>3+</sup> doped Sb<sub>2</sub>O<sub>3</sub>-PbO-ZnO-MO (CaO,SrO & BaO)

glasses. The coordinates are for BaSbZDy, CaSbZDy & SrSbZDy glasses from top to bottom.

#### IV. CONCLUSIONS

The optical absorption, photoluminescence spectra of Dy<sup>3+</sup> in MO (BaO, CaO, & SrO)–PbO–ZnO–Sb<sub>2</sub>O<sub>3</sub> glasses have been investigated. The Judd-Ofelt theory is applied to characterize the optical absorption spectra of these ions for all the three glass systems. Among the three J-O parameters ( $\Omega_2$ ), the value of  $\Omega_2$  which is related to the structural changes in the vicinity of the Dy<sup>3+</sup> ion is found to be the lowest for BaO mixed glasses. The radiative transition probabilities and branching ratios evaluated for various luminescent transitions were observed to be the largest for the glasses mixed with BaO mixed glasses. Comparatively low non-radiative losses for BaO mixed glasses among the three glasses are found to be the reason for the high luminescence efficiency of these glasses. These facts were explained using IR spectral studies.

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