# Spectral and Thermal Properties of $Ho^{3+}$ Doped Aluminum- Barium- Calcium-Magnesium Fluoride Glasses

S.L.Meena

*Ceremic Laboratory, Department of physics, Jai Narain Vyas University, Jodhpur 342001(Raj.) India*

***Abstract***

*Aluminum- Barium- Calcium-Magnesium Fluoride glasses containing $Ho^{3+}$in (45- x):$AlF_2$:15 $BaF_2$:15 $CaF_2$: 25 $MgF_2$: $xHo_2O_3$ (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by x-ray diffraction studies. Optical absorption spectra were recorded at room temperature for all glass samples. The experimental oscillator strengths were calculated from the area under the absorption bands. Slater-Condon parameter ($F_2$), Lande's parameter ($\xi_{4f}$), Nephlauxetic ratio ($\beta'$) and Bonding parameter ($b^{½}$) have been computed. Using these parameters energies and intensities of these bands has been calculated. Judd-Ofelt intensity parameters $\Omega_\lambda$ ($\lambda$=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross–section of various emission lines have been evaluated.*

**Keywords:** *ABCMF Glasses, Optical Properties, Judd-Ofelt Theory, Rare earth ions.*

## I. INTRODUCTION

Aluminum- Barium- Calcium-Magnesium Fluoride glasses find a wide range of technological applications as electro-chemical devices as ionic conductors, optoelectronic devices [1-3]. The glasses containing rare earth in various forms such as network formers, modifiers or luminescent ions are of great deal of interest for their unique optical, electrical and magnetic properties [4, 5].The oxide glasses generally possess a good mechanical strength, chemical durability, and thermal stability while the heavy-metal fluorides possess a low vibrational energy, resulting in an increased up conversion efficiency of the incorporated rare-earth ions [6-8].

Among all, fluoride glasses have been a subject of interest in the investigation of passive and active optical applications including optical waveguides, optical amplifiers, and laser hosts materials. Due to low coupling of the rare earth (RE) with the host vibrations, which moderates the nonradiative emission from the excited electronic level and therefore increases the quantum efficiency of the emitting level. The past literature shows that the rare earth ions find more important application in the preparation of the laser materials [9-12].

In this work, we have studied on the absorption and emission properties of $Ho^{3+}$ doped Aluminum- Barium-Calcium-Magnesium Fluoride glasses. The Judd-Ofelt theory has been applied to compute the intensity parameters $\Omega_\lambda$ ($\lambda$=2, 4, 6), which are sensitive to the environment of rare earth ion. From these parameters, important optical properties such as radiative transition probability for spontaneous emission, radiative lifetime of the excited states and branching ratio can be estimated.

## II. EXERIMENT TECHNIQUES

### *Preparatin of glasses*

The following $Ho^{3+}$ doped Aluminum- Barium-Calcium-Magnesium Fluoride glass samples (45-x):$AlF_2$:15 $BaF_2$:15 $CaF_2$: 25 $MgF_2$: $xHo_2O_3$ (where x=1, 1.5.2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of $AlF_2$, $BaF_2$ $CaF_2$, $MgF_2$and $Ho_2O_3$. All weighed chemicals were powdered by using an Agate pestle mortar and mixed thoroughly before each batch (10g) was melted in alumina crucibles in silicon carbide based an electrical furnace.

Silicon Carbide Muffle furnace was heated to working temperature of $1000^0$C, for preparation of Aluminum- Barium-Calcium-Magnesium Fluoride glasses, for two hours to ensure the melt to be free from gases. The melt was stirred several times to ensure homogeneity. For quenching, the melt was quickly poured on the steel plate & was immediately inserted in the muffle furnace for annealing. The steel plate was preheated to$100^0$C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of $200^0$C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in

**Table 1**

**Table 1 Chemical composition of the glasses**

| Sample | Glass composition (mol %) |
|---|---|
| ABCMF (UD) | 45:$AlF_2$:15 $BaF_2$:15 $CaF_2$: 25 $MgF_2$ |
| ABCMF (HO1) | 44:$AlF_2$:15 $BaF_2$:15 $CaF_2$: 25 $MgF_2$: 1 $Ho_2O_3$ |
| ABCMF (HO1.5) | 43.5:$AlF_2$:15 $BaF_2$:15 $CaF_2$: 25 $MgF_2$: 1.5 $Ho_2O_3$ |
| ABCMF (HOO2) | 43:$AlF_2$:15 $BaF_2$:15 $CaF_2$: 25 $MgF_2$: 2 $Ho_2O_3$ |
| ABCMF (UD)— | Represents undoped Aluminum- Barium-Calcium-Magnesium Fluoride glass specimens |
| ABCMF (HO) - | Represents $Ho^{3+}$ doped Aluminum- Barium-Calcium-Magnesium Fluoride glass specimens |

## III. THEORY

### *A. Oscillator Strength*

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [13].

$$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon (\nu)\, d\nu \qquad (1)$$

where, $\varepsilon(\nu)$ is molar absorption coefficient at a given energy $\nu$ ($cm^{-1}$), to be evaluated from Beer–Lambert law.

Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated, using the modified relation [14].

$$P_m = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\upsilon_{1/2} \qquad (2)$$

where c is the molar concentration of the absorbing ion per unit volume, I is the optical path length, $\log I_0/I$ is absorbtivity or optical density and $\Delta\upsilon_{1/2}$ is half band width.

### *B. Judd-Ofelt Intensity Parameters*

According to Judd [15] and Ofelt [16] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N (S, L) J\rangle$ level and the terminal J' manifold $|4f^N (S', L') J'\rangle$ is given by:

$$\frac{8\Pi^2 mc\bar{\upsilon}}{3h(2J+1)}\frac{1}{n}\left[\frac{(n^2+2)^2}{9}\right] \times S(J,J') \qquad (3)$$

where, the line strength S (J, J') is given by the equation

$$S(J, J') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N(S, L) J \| U^{(\lambda)} \| 4f^N (S', L') J'\rangle^2 \qquad (4)$$

In the above equation m is the mass of an electron, c is the velocity of light, $\nu$ is the wave number of the transition, h is Planck's constant, n is the refractive index, J and J' are the total angular momentum of the initial and final level respectively, $\Omega_\lambda$ ($\lambda$ = 2, 4, 6) are known as Judd-Ofelt intensity parameters.

### *C. Radiative Properties*

The $\Omega_\lambda$ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time ($\tau_R$), and laser parameters like fluorescence branching ratio ($\beta_R$) and stimulated emission cross section ($\sigma_p$).

The spontaneous emission probability from initial manifold $|4f^N (S', L') J'\rangle$ to a final manifold $|4f^N (S, L) J\rangle$| is given by:

$$A[(S', L') J'; (S, L) J] = \frac{64\pi^2\nu^3}{3h(2J'+1)}\left[\frac{n(n^2+2)^2}{9}\right] \times S(J', \bar{J})$$
(5)

Where, $S(J', J) = e^2 [\Omega_2 \| U^{(2)} \|^2 + \Omega_4 \| U^{(4)} \|^2 + \Omega_6 \| U^{(6)} \|^2]$

The fluorescence branching ratio for the transitions originating from a specific initial manifold $|4f^N (S', L') J'\rangle$ to a final many fold $|4f^N (S, L) J\rangle$ is given by

$$\beta [(S', L') J'; (S, L) J] = \sum_{SLJ} \frac{A[(S' L)]}{A[(S' L') J' (\bar{S} L)]} \quad (6)$$

where, the sum is over all terminal manifolds.
The radiative life time is given by

$$\tau_{rad} = \sum_{SLJ} A[(S', L') J'; (S,L)] = A^{-1}_{Total} \quad (7)$$

where, the sum is over all possible terminal manifolds. The stimulated emission cross -section for a transition from an initial manifold $|4f^N (S', L') J'\rangle$ to a final manifold $|4f^N (S, L) J\rangle|$ is expressed as

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right] \times A[(S', L') J'; (\bar{S}, \bar{L})\bar{J}] \quad (8)$$

where, $\lambda_p$ the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width.

### *D. Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$)*

The nature of the R-O bond is known by the Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$), which are computed by using following formulae [17, 18]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{\nu_g}{\nu_a} \quad (9)$$

where, $\nu_a$ and $\nu_g$ refer to the energies of the corresponding transition in the glass and free ion, respectively. The values of bonding parameter ($b^{1/2}$) are given by

$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \quad (10)$$

## IV. RESULT AND DISCUSSION

### *A. XRD Measurement*

Figure 1 presents the XRD pattern of the samples containing show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

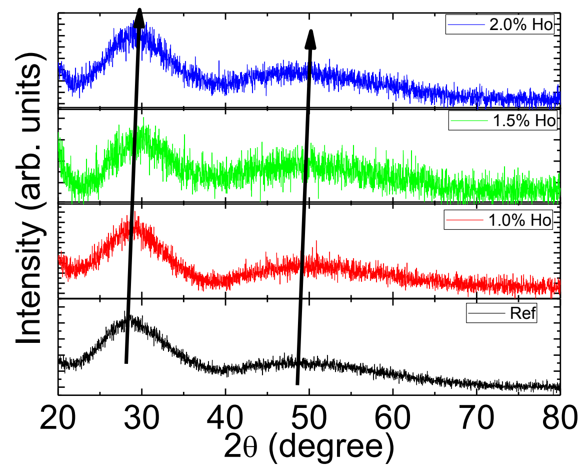
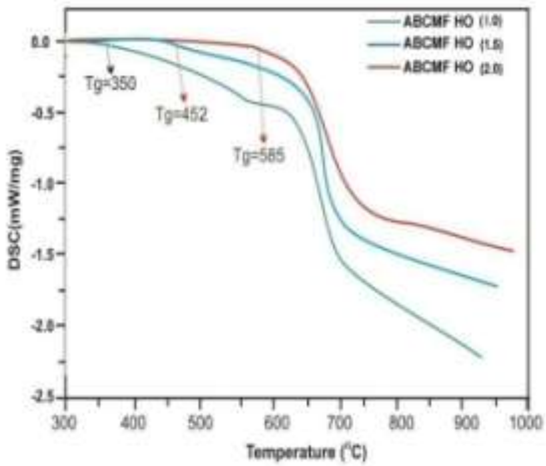



**Fig.1: X-ray diffraction pattern of ABCMF (HO) glasses.**

### *B. Thermal Properties*

Figure 2 shows the thermal properties of ABCMF glass from 300$^0$C to 1000$^0$C. From the DSC curve of present glasses system, we can find out that no crystallization peak is apparent and the glass transition temperature $T_g$ are 350$^0$C, 452$^0$C and 585$^0$C respectively. The $T_g$ increase with the contents of $Ho_2O_3$ increase. We could conclude that thermal properties of the ABCMF glass are good for fiber drawing from the analysis of DSC curve.




### *C. Absorption spectra*

The absorption spectra of ABCMF (HO) glasses, consists of absorption bands corresponding to the absorptions from the ground state $^5I_8$ of $Ho^{3+}$ ions. Twelve absorption bands have been observed from the ground state $^5I_8$ to excited states $^5I_5$, $^5I_4$, $^5F_5$, $^5F_4$, $^5F_3$, $^3K_8$, $^5G_6$, $(5G,3G)_5$, $^5G_4$, $^5G_2$, $^5G_3$, and $^3F_4$ for $Ho^{3+}$ doped ABCMF (HO) glasses.

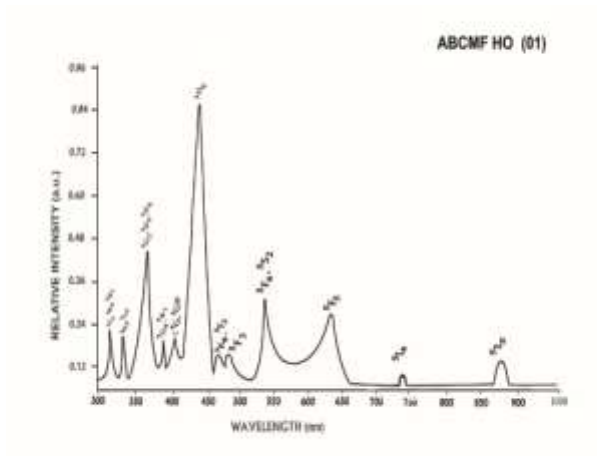



**Fig.2: UV-VIS absorption spectra of ABCMF (HO) glasses.**

The experimental and calculated oscillator strengths for $Ho^{3+}$ ions in Aluminum- Barium-Calcium-Magnesium Fluoride glasses are given in **Table 2**

**Table 2. Measured and calculated oscillator strength ($P^m \times 10^{+6}$) of $Ho^{3+}$ ions in ABCMF glasses.**

| Energy level | Glass ABCMF (HO 01) | | Glass ABCMF (HO 1.5) | | Glass ABCMF (HO 02) | |
|---|---|---|---|---|---|---|
| | $P_{exp.}$ | $P_{cal.}$ | $P_{exp.}$ | $P_{cal.}$ | $P_{exp.}$ | $P_{cal.}$ |
| $^5I_5$ | 0.36 | 0.24 | 0.32 | 0.235 | 0.28 | 0.23 |
| $^5I_4$ | 0.042 | 0.022 | 0.036 | 0.022 | 0.028 | 0.021 |
| $^5F_5$ | 3.38 | 2.714 | 3.32 | 2.687 | 3.25 | 2.64 |
| $^5F_5$, $^5S_2$ | 4.52 | 4.232 | 4.48 | 4.192 | 4.42 | 4.121 |
| $^5F_3$ | 1.55 | 2.36 | 1.51 | 2.338 | 1.46 | 2.30 |
| $^3K_8$, $^5F_2$ | 1.35 | 1.94 | 1.30 | 1.916 | 1.25 | 1.875 |
| $^5G_6$ | 25.25 | 25.29 | 24.42 | 24.49 | 23.35 | 23.437 |
| $(^5G, ^3G)_5$ | 3.58 | 1.62 | 3.52 | 1.60 | 3.48 | 1.570 |
| $^5G_4$, $^3K_7$ | 0.06 | 0.60 | .056 | 0.589 | 0.048 | 0.576 |
| $^5G_2$, $^3H_5$ | 5.38 | 5.37 | 5.32 | 5.217 | 5.28 | 5.016 |
| $^5G_3$, $^3L_9$ | 1.41 | 1.37 | 1.36 | 1.35 | 1.32 | 1.317 |
| $^3F_4$, $^3K_6$ | 1.28 | 4.01 | 1.25 | 3.957 | 1.21 | 3.886 |
| R.m.s.deviation | | 1.0457 | | 1.0360 | | 1.0298 |

Computed values of $(F_2)$, Lande's parameter $(\xi_{4f})$, Nephlauxetic ratio**(**β') and bonding parameter $(b^{½})$ for $Ho^{3+}$ doped ABCMF glass specimen are given in **Table 3**.

**Table 3. $F_2$, $\xi_{4f}$, β' and $b^{½}$ parameters for Holmium doped glass specimen.**

| Glass Specimen | $F_2$ | $\xi_{4f}$ | β' | $b^{½}$ |
|---|---|---|---|---|
| $Ho^{3+}$ | 427.89 | 2196.01 | 0.9718 | 0.1187 |

Judd-Ofelt intensity parameters $\Omega_\lambda$ ($\lambda$ = 2, 4, 6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions. In the present case the three $\Omega_\lambda$ parameters follow the trend $\Omega_4 < \Omega_6 < \Omega_2$. The values of Judd-Ofelt intensity parameters are given in **Table 4**.

**Table 4. Judd-Ofelt intensity parameters for $Ho^{3+}$ doped ABCMF glass specimens.**

| Glass Specimen | $\Omega_2(pm^2)$ | $\Omega_4(pm^2)$ | $\Omega_6(pm^2)$ | $\Omega_4/\Omega_6$ | Ref. |
|---|---|---|---|---|---|
| ABCMF (HO 01) | 5.739 | 1.183 | 1.987 | 0.5954 | P.W. |
| ABCMF (HO 1.5) | 5.528 | 1.166 | 1.968 | 0.5925 | P.W. |
| ABCMF (HO 02) | 5.254 | 1.145 | 1.933 | 0.5923 | P.W. |
| Oxyfluoride glass | 6.41 | 1.02 | 2.25 | 0.453 | [19] |
| $Ba_2TiSi_2O_3$:Crystal | 4.97 | 0.60 | 0.68 | 0.652 | [20] |
| ZFBP | 1.347 | 0.66 | 0.92 | 0.717 | [21] |

### *D. Fluorescence Spectrum*

The fluorescence spectrum of $Ho^{3+}$ doped in Aluminum- Barium-Calcium-Magnesium Fluoride glass is shown in Figure 3. There are two broad bands ($^5F_4, {}^5S_2 \rightarrow {}^5I_8$) and ($^5F_5 \rightarrow {}^5I_8$) respectively for glass specimens.

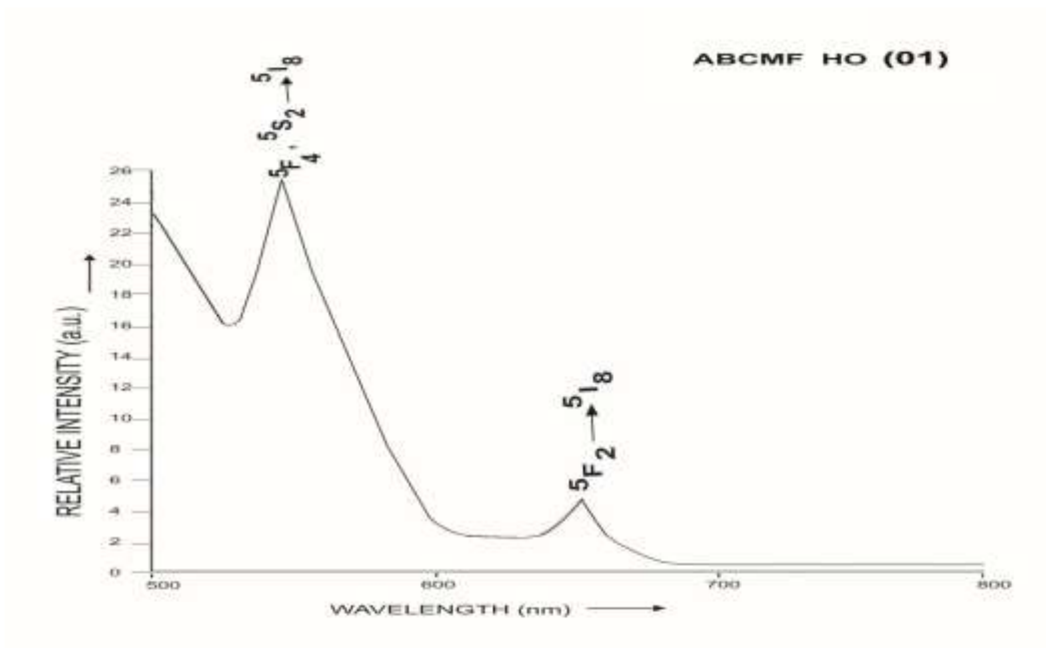



**Fig.3: Fluorescence spectrum of ABCMF glasses doped with $Ho^{3+}$.**

**Table 5. Emission peak wave lengths ($\lambda_p$), radiative transition probability ($A_{rad}$), branching ratio ($\beta_R$), stimulated emission cross-section ($\sigma_p$), and radiative life time ($\tau_R$) for various transitions in $Ho^{3+}$ doped ABCMF glasses.**

**GLASS ABCMF (HO 01)**

| Transition | $\lambda_p$(nm) | $A_{rad}(s^{-1})$ | $\beta_R$ | $\sigma_p$ ($10^{-20}cm^2$) | $\tau_R$( µs) |
|---|---|---|---|---|---|
| $^5F_4, {}^5S_2 \rightarrow {}^5I_8$ | 555 | 5339.92 | 0.7218 | 1.103 | 135.17 |
| $^5F_5 \rightarrow {}^5I_8$ | 652 | 2058.37 | 0.2782 | 1.072 | |

**GLASS ABCMF (HO 1.5)**

| Transition | $\lambda_p$(nm) | $A_{rad}(s^{-1})$ | $\beta_R$ | $\sigma_p$ ($10^{-20}cm^2$) | $\tau_R$( µs) |
|---|---|---|---|---|---|
| $^5F_4, {}^5S_2 \rightarrow {}^5I_8$ | 555 | 5295.72 | 0.7220 | 1.087 | 136.34 |
| $^5F_5 \rightarrow {}^5I_8$ | 652 | 2038.65 | 0.2780 | 1.054 | |

**GLASS ABCMF (HO 02)**

| Transition | $\lambda_p$(nm) | $A_{rad}(s^{-1})$ | $\beta_R$ | $\sigma_p$ ($10^{-20}cm^2$) | $\tau_R$( µs) |
|---|---|---|---|---|---|
| $^5F_4, {}^5S_2 \rightarrow {}^5I_8$ | 555 | 5205.84 | 0.7219 | 1.058 | 138.68 |
| $^5F_5 \rightarrow {}^5I_8$ | 652 | 2005.22 | 0.2781 | 1.022 | |

## V. CONCLUSION

In the present study, the glass samples of composition (45- x):$AlF_2$:15 $BaF_2$:15 $CaF_2$: 25 $MgF_2$: x$Ho_2O_3$ (where x =1, 1.5, 2 mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section ($\sigma_p$) is found to be maximum for the transition ($^5F_4, {}^5S_2 \rightarrow {}^5I_8$) for glass ABCMF (HO 01), suggesting that glass ABCMF (HO 01) is better compared to the other two glass systems ABCMF (HO 1.5) and ABCMF (HO 02).

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