Energy Transfer Studies in Dy³⁺ Ions Doped Aluminium Telluroborate Glasses

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Abstract

Dy³⁺ ions doped aluminium telluroborate glasses were prepared following the melt-quenching technique by varying the Dy³⁺ ions concentration with respect to borate content. The optical behavior of the title glasses was explored by recording absorption and luminescence spectra. The ionic or covalent nature was determined from the energy positions observed in the absorption spectra using Nephelauxetic ratios. The Yellow/Blue ratio was calculated from the luminescence spectra to determine the degree of asymmetry in the prepared glasses. The luminescence intensity is found to quench beyond 1.0 wt% of Dy³⁺ ions doped aluminium telluroborate glass which may be due to the resonance energy transfer or cross-relaxation phenomena takes place and is analyzed with Inokuti-Hirayama model.

Keywords: Glasses, Absorption, Luminescence, Energy transfer, Decay Analysis

1. Introduction

Rare earth doped materials finds applications in various fields such as solid state lasers, upconvertors, optical memories, white light emitting diodes, optical amplifiers due to their sharp emission, high stability and long lifetime [1]. Among them, Dy³⁺ ions find applications in white LEDs due to its dominant emission from $^4F_{9/2} \rightarrow ^6H_{15/2}$ (484 nm), $^4F_{9/2} \rightarrow ^6H_{13/2}$ (576 nm) transitions whose integrated intensity ratio can be tuned with ligand field environment. Many researchers such as Venkata Krishnaiah et al. [2], Joanna Pisarska et al. [3] studied the optical properties of Dy³⁺ ions in various host matrices and discussed the energy transfer mechanism involved in it. In the present work, energy transfer mechanism involved in the Dy³⁺ ions doped aluminum telluroborate glasses were studied with luminescence, decay spectral analysis and their results were discussed and compared with the reported literature.

2. Experimental

Dy³⁺ ions doped aluminium telluroborate glasses were prepared with the chemical composition (55–x)H_3BO_3+25TeO_2+20Al_2O_3+xDy_2O_3 (where x =0.25, 0.5, 1.0, 2.0 in wt%) following the melt-quenching technique [4] and labeled as ATB0.25D, ATB0.5D, ATB1.0D, ATB2.0D respectively. High Purity (99.99%) chemicals (H_3BO_3, TeO_2, Al_2O_3, Dy_2O_3) from Sigma Aldrich were used as precursors for the preparation of these glass samples. The absorption spectral measurements were made using CARY 500 UV-Vis-NIR spectrophotometer in the wavelength region 300–2000 nm with a spectral resolution of ± 1 nm. The Luminescence spectra have been recorded employing JASCO spectrofluorimeter using xenon lamp (450 W) in the wavelength range 400–700 nm with a spectral resolution of ± 1 nm. The decay measurements were made employing the Edinburgh FLS–900 time resolved fluorescence spectrometer.

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3. Absorption spectra

The absorption spectra of the Dy^{3+} ions doped aluminium telluroborate glasses were recorded in the wavelength region 300–2000 nm. Since there is no much variation in the spectral position with the increase in the concentration of Dy^{3+} ions in the prepared glasses, absorption spectrum of the ATB2.0D glass is shown in figure 1 as a representative case and the band assignments to the observed energy positions were made referring the literature reported by Carnal et al. [5] and is comparable to the reported literature [1,6]. The absorption edge was found to be red shifted with the increase in the concentration of the Dy^{3+} ions in the prepared glasses. Twelve inhomogeneously broadened peaks were observed due to the disorderliness present in the title glasses from the $^6H_{15/2}$ ground state to the various excited states such as $^6P_{7/2}$, $^6P_{5/2}$, $^4F_{7/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}$, $^6H_{11/2}$ positioning at 346, 365, 388, 425, 450, 470, 750, 800, 902, 1092 nm respectively. Among these transitions, $^6H_{15/2} \rightarrow {}^6F_{5/2}$ transition obeys the selection rule $\Delta J \leq 2$, $\Delta L \leq 2$, $\Delta S = 0$ and its intensity varies with the increase in the concentration of Dy^{3+} ions in the prepared glasses hence this transition is regarded as hypersensitive transition. From the energy positions of the absorption spectra, the covalancy nature was determined using Nephelauxetic ratios and bonding parameter values obtained by using the expressions reported in the literature [1] and the values are found to be − 0.0057, − 0.0056, − 0.0053, − 0.0051 corresponding to the prepared ATB0.25D, ATB0.5D, ATB1.0D, ATB2.0D glasses respectively.
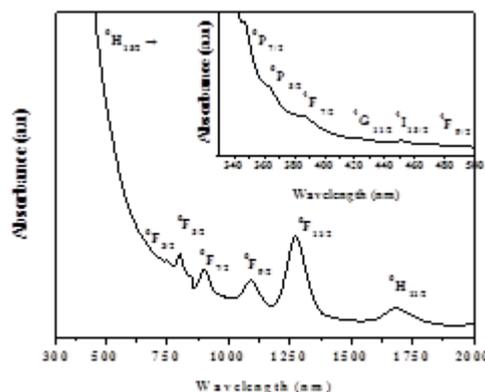

Figure 1. Absorption spectrum of 2.0 wt% of Dy^{3+} ion doped aluminium telluroborate glass

4. Excitation and emission spectra

Figure 2 shows the representative excitation spectrum of the ATB2.0D glass recorded in the wavelength region 250–500 nm by monitoring the emission at 484 nm and 575 nm. Eight excitation peaks were observed from the $^6H_{15/2}$ ground state to the various excited states $^6P_{3/2}$, $({}^4F, {}^4D)_{5/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4F_{7/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$ positioning at 325, 338, 350, 365, 388, 426, 452, 473 nm respectively.
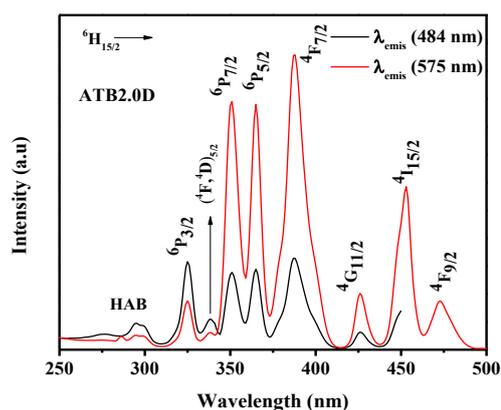

Figure 2. Excitation spectrum of ATB2.0D glass

Among them, peak corresponding to the $^6H_{15/2} \rightarrow {}^4F_{7/2}$ (388 nm) transition possess comparatively higher intensity for both the emission wavelengths thus suggest the fact that the prepared glasses can

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effectively be excited at 388 nm. The same excitation wavelength is chosen to record the luminescence spectra for all the prepared glasses and is shown in figure 3. Three distinguishable emission peaks were observed at 483, 575, 662 nm corresponding to the $^4F_{9/2} \to {}^6H_{15/2}$, $^4F_{9/2} \to {}^6H_{13/2}$, $^4F_{9/2} \to {}^6H_{11/2}$ transitions respectively. Among them, $^4F_{9/2} \to {}^6H_{13/2}$ transition possesses higher intensity compared to the other transitions which occurs due to the interaction of electric dipole with photons whereas the $^4F_{9/2} \to {}^6H_{15/2}$ transition occurs due to the interaction of magnetic dipole with photons. The ratio between these two transitions ($^4F_{9/2} \to {}^6H_{13/2}$ and $^4F_{9/2} \to {}^6H_{15/2}$) act as a local field sensor because the intensity of the former transition depends upon crystal field while the later does not and the values were found to be 1.65, 1.91, 1.96, 1.76 for the present ATB0.25D, ATB0.5D, ATB1.0D, ATB2.0D glasses respectively. From these values it is confirmed that the aluminium telluroborate glass with 1.0 wt % Dy^{3+} ions concentration occupies higher asymmetry environment compared to the other prepared glasses.

Table 1. Observed band positions (cm^{-1}) and bonding parameters ($\bar{\beta}$ and δ) of the Dy^{3+} ions doped aluminium telluroborate glasses

Transition $^6H_{15/2} \to$	ATB 0.25D	ATB 0.5D	ATB 1.0D	ATB 2.0D	Aquo ion [2]
$^6H_{11/2}$	5945	5959	5906	5924	5850
$^6F_{11/2}$	7855	7825	7856	7823	7700
$^6F_{9/2}$	9124	9134	9141	9149	9100
$^6F_{7/2}$	11109	11060	11084	11106	11000
$^6F_{5/2}$	12505	12496	12463	12486	12400
$^6F_{3/2}$	13205	13336	13303	13298	13250
$^4F_{9/2}$	21110	21100	21101	21020	21100
$^4I_{15/2}$	22057	22047	22119	22126	22100
$^4G_{11/2}$	23514	23524	23534	23407	23400
$^4F_{7/2}$	25889	25839	25824	25807	25800
$^6P_{5/2}$	27293	27273	27367	27351	27450
$^6P_{7/2}$	28888	28838	28745	28858	28550
$\bar{\beta}$	1.0057	1.0056	1.0053	1.0051	-
δ	−0.0057	−0.0056	−0.0053	−0.0051	-

The luminescence intensity is found to quench beyond 1.0 wt% Dy^{3+} ion content glass and the same may be attributed to the resonance energy transfer or cross-relaxation mechanism which takes place as shown below [4].
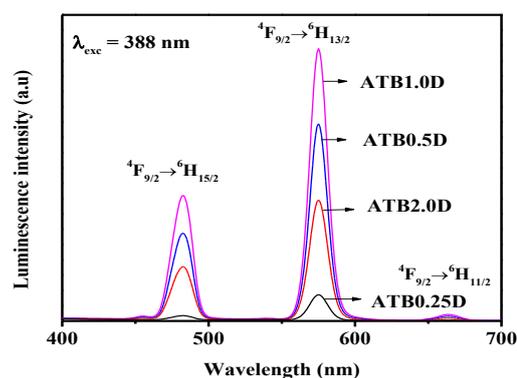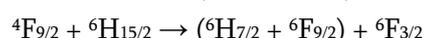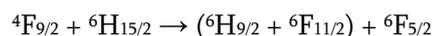
$$^4F_{9/2} + {}^6H_{15/2} \to ({}^6H_{9/2} + {}^6F_{11/2}) + {}^6F_{5/2}$$
$$^4F_{9/2} + {}^6H_{15/2} \to ({}^6H_{7/2} + {}^6F_{9/2}) + {}^6F_{3/2}$$

Figure 3. Emission spectra of Dy^{3+} ion doped aluminium telluroborate glasses

Resonance energy transfer takes place when the excitation and emission spectra overlaps and is shown in figure 4 for the $^4F_{9/2}$, $^6H_{15/2}$ state. The partial energy level diagram depicting these processes is shown in figure 5. When Dy^{3+} ion is excited to the $^4F_{7/2}$ energy level (388 nm), it non-radiatively decays to the $^4F_{9/2}$ energy level where from radiative transition takes place between ($^4F_{9/2}$, $^6H_{15/2}$), ($^4F_{9/2}$, $^6H_{13/2}$), ($^4F_{9/2}$, $^6H_{11/2}$) states. Due to the large energy gap between the $^4F_{9/2}$ level to the next lower energy level (~ 7000 cm^{-1}) multiphonon relaxation is less dominant where more number of phonons is required and the luminescence intensity quenches due to the above mentioned resonance energy transfer or cross-relaxation phenomenon.
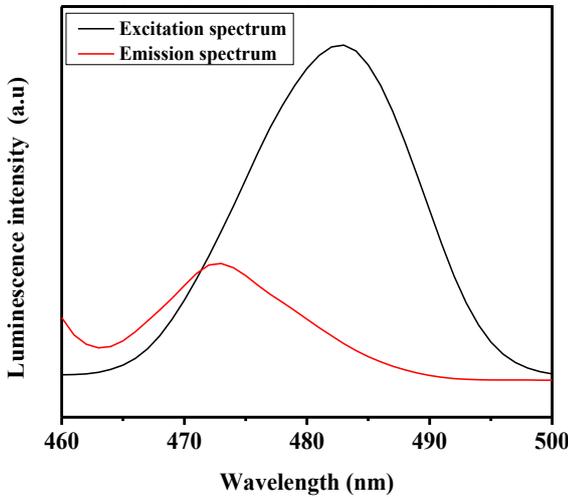
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Figure 4. Resonance energy transfer for ($^4F_{9/2}$, $^6H_{15/2}$) state
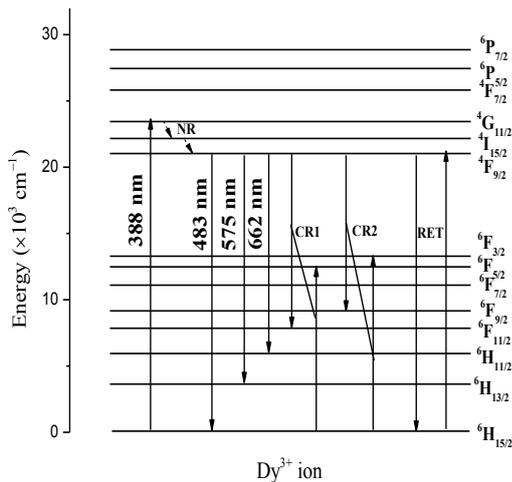

Figure 5. Partial energy diagram of Dy^{3+}ion doped aluminum doped glass

The strength of the luminescence intensity is measured through lifetime measurements recorded by monitoring an excitation at 388 nm and emission at 575 nm and is shown in figure 6. The decay curves were fitted following the below given bi-exponential function.

$$I = a_1 \exp(-x/t_1) + a_2 \exp(-x/t_2)$$

and the average lifetime (τ) values were calculated using the following expression

$$\tau = \frac{a_1 t_1^2 + a_2 t_2^2}{a_1 t_1 + a_2 t_2}$$

These values were found to decrease from 0.53 to 0.28 ms with the increase in the concentration of Dy^{3+} ions in the prepared glasses and the same is due to the increasing energy transfer process takes place between Dy^{3+}–Dy^{3+} ions.
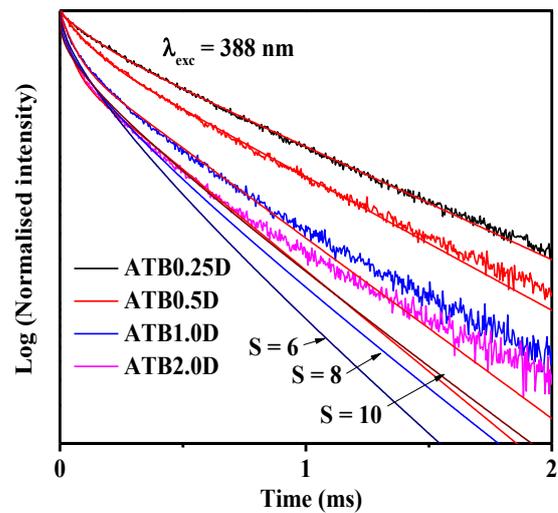

Figure 6. Decay curve of Dy^{3+} ions doped aluminium telluroborate glasses

These decay curves were fitted through Inokuti-Hirayama model [7] to determine type of interaction involved using the following expression

$$I(t) = I_0 \exp\left[\left(-\frac{t}{t_0}\right) - q\left(\frac{t}{t_0}\right)^{3/3}\right]$$

where 't' is the time after pulsed excitation, t_0 is the intrinsic decay time of the donor in the absence of acceptors. The value of S (=6, 8, 10) determine the dominant interaction is of dipole-dipole, dipole-quadrupole, quadrupole-quadrupole type and the model is well fitted for S = 6 thus suggests the fact that the dipole-dipole interaction is dominant. Other parameters such as forster distance, donor-acceptor interaction were calculated using the expressions reported in the literature [8] and the

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values were shown in table 2 along with the reported literature [1,6,8].

Table 2. Experimental lifetime (τ_{exp}, ms), donor-acceptor interaction parameter (C_{DA}, $\times 10^{-42}$ cm^6/s), critical distance (R_0, $\times 10^{-8}$ cm), energy transfer parameter (q) for Dy^{3+} ions doped aluminium telluroborate glasses under 388 nm excitation for the emission energy level $^4F_{9/2}$, $^6H_{13/2}$

Glass Code	τ_{exp}	q	C_{DA}	R_0
ATB0.25D	0.53	0.16	14.09	4.26
ATB0.5D	0.43	0.59	57.53	5.38
ATB1.0D	0.31	1.26	75.29	5.63
ATB2.0D	0.28	1.62	50.34	5.26
PKAZLFDy [1]	0.62	0.71	1.32	69.5
PKAND[6]	0.47	0.86	2.15	7.31
TBZnD [8]	0.41	0.65	2.42	6.9

5. Conclusion

Optical and energy transfer behavior of the Dy^{3+} ions doped title glasses have been studied and reported. The bonding parameter studies exhibits the ionic nature. Luminescence quenching has been experienced for glasses having Dy^{3+} ions concentration beyond 1 wt% and is due to RET and cross-relaxation process. The decay of the $^4F_{9/2}$ excited level is found to be single exponential for lower concentration and turns out to be non-exponential for higher concentration of Dy^{3+} ions in the prepared glasses. The non-exponential behaviour of the decay curve analysis through Inokuti-Hirayama model indicates that the energy transfer between Dy^{3+} ions is of dipole-dipole nature.

6. References

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