Dy^{3+} Doped Glasses For White Light Applications : A Short Review

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Abstract: Recently published various Dy^{3+} ions doped glass materials were taken for analysis to understand their white light emission behavior and to correlate that behavior with their optical properties. The structural properties of the materials were analyzed using their Judd-Ofelt (J-O) intensity parameters. All the selected glasses have shown covalent nature for the Dy^{3+}-Oxygen bond and low symmetry around Dy^{3+} ion sites. The colour coordinates (X, Y) which are crucial in understanding white light behavior have found a relation with the optical property stimulated emission cross-section of the selected glasses. The glasses with higher σ_{se} values have the colour coordinates of X and Y > 0.4 which are far from the standard colour coordinates (X=0.333, Y=0.333) and the glasses with lesser σ_{se} values have the colour coordinates of X and Y < 0.4 which are nearer to the standard colour coordinates (X=0.333, Y=0.333).

Index Terms: Colour coordinates, Covalent nature, Dy^{3+} ions doped glasses, Judd-Ofelt intensity parameters, Low symmetry, Stimulated emission cross-section, Y/B ratio.

1. INTRODUCTION

Under the Solid-State Lightening (SSL) devices category, Dy^{3+} ions doped glasses have been investigating for white light emitting material applications as the SSL devices have enormous advantages in the field of lightening devices such as low energy consumption, ease of control, small in size, reduced carbon emission, unidirectional distribution, cool beam and colour rendering that can be very high and comparable to high fluorescent lamps with high colour rendering index (CRI), long life and high performance in cold environmental conditions etc. [1-9]. Among the available Rare Earth (RE) ions, especially Dy^{3+} ion can produce white light through combination of its intense yellow and blue emissions. The yellow to blue intensity (Y/B) ratio from emission transitions $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (electric dipole) and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (magnetic dipole) of Dy^{3+} ions in a glass system can influence the quality of emitting white light from the glass material [10-12]. Particularly, the intensity of the hypersensitive emission transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ which obeys the selection rule $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$ depends on the nature of the glass system and the ligand environment around the Dy^{3+} ion in that glass system. So, the generation of white light from Dy^{3+} ions doped glasses can be manipulated or tuned by altering the combinations of chemical compositions of the glass system [10-15].

As the white light emission from Dy^{3+} glasses can be greatly altered by the selected glass composition, we have vast variety of glass bases to tailor the white light emission from Dy^{3+} ions [1,8,16-25]. The glasses like Borate glasses, Phosphate glasses, Silicate glasses, Boro-Silicate glasses, Oxide glasses, Oxyfluoride glasses, Tellurite glasses, Boro-Tellurite glasses, Boro-Aluminate glasses etc. have their own advantages as well as disadvantages in case of properties like Phonon energy, Optical stability, Chemical durability, Physical strength etc [9,11,26-30]. In this study, we have selected a set of available Dy^{3+} ions doped glasses from the literature to analyse the white light emission capabilities with help of their optical properties and to compare them with our earlier study of AEBTDy1.0 glass [1].

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2 METHOD OF SYNTHESIS

All the glasses that are chosen for this analysis are prepared by simple conventional melt quenching technique. In melt quenching technique the glasses are usually prepared by melting the homogeneous mixture of selected chemical compositions in an electrical furnace and after air quenching the melts by pouring on to the pre heated moulds.

3 ANALYSIS OF DIFFERENT DY^{3+} DOPED GLASSES FOR WHITE LIGHT APPLICATIONS

A set of glasses doped with Dy^{3+} ions from various published studies are taken to compare their fitness as white light emitting materials with our recently published AEBTDy1.0 glass [1].

The selected glass compositions for this analysis are as follows:

AEBTDy1.0 [1] = $60B_2O_3$-$15TeO_2$-9CaO-5MgO-$5Al_2O_3$-$5TiO_2$-$1Dy_2O_3$ (Alkaline-Earth Boro Tellurite glass)

G2 glass [2] = $20La_2O_3$-$10CaF_2$-$69P_2O_5$-$1Dy_2O_3$ (Lanthanum Calcium Phosphate oxyfluoride glass)

BPB0.5D [3] = $30B_2O_3$-$24.5P_2O_5$-$5Al_2O_3$-10PbO-$10ZnF_2$-$20Bi_2O_3$-$0.5Dy_2O_3$ (Oxyfluoro-borophosphate glass)

TZKCDy05 [4] = $61.5TeO_2$-25ZnO-$8K_2O$-5CaO-$0.5Dy_2O_3$ (Tellurite glass)

TBZnD [5] = $30TeO_2$-$29.5B_2O_3$-20ZnO-$20ZnF_2$-$0.5Dy_2O_3$ (Telluroborate Glass)

LBGS-0.5Dy [6] = $40Li_2O$-05BaO-$05Gd_2O_3$-$49.5SiO_2$-$0.5Dy_2O_3$ (LBGS glass)

BGGD1.00 [7] = $30B_2O_3$-$40GeO_2$-$29Gd_2O_3$-$1Dy_2O_3$ (Gadolinium Borogermanate glass)

Dy:BaAS [8] = 35BaO-$10Al_2O_3$-$55SiO_2$: 1×10^{20} Dy^{3+}/cm^3 (Alkaline-Earth Aluminosilicate glass)

TBZDy0.5 [9] = $69.5TeO_2$-$20B_2O_3$-10ZnO-$0.5Dy_2O_3$ (Zinc Borotellurite glass)

Glass B [10] = $10Li_2O$-10PbO-$9.5Al_2O_3$-$70B_2O_3$-$0.5Dy_2O_3$ (Lithium Lead Alumino Borate glass)

BPA0.5D [11] = $45H_3BO_3$-$24.5H_6NO_4P$-$15K_2CO_3$-$10ZnF_2$-

$5Al_2O_3$-$0.5Dy_2O_3$ (Aluminofluoroborophosphate glass)
BiNFB0.5D [12] = $41B_2O_3$-$20Bi_2O_3$-$19.5Na_2O$-$19CaF_2$-$0.5Dy_2O_3$ (Bismuth Sodiumfluoroborate glass)
Various properties of the above-mentioned glasses are tabulated in Table.1 and Table.2.

TABLE 1
Judd-Ofelt (J-O) intensity parameters (Ω_λ X 10^{-22} cm^2, λ= 2, 4, 6) and their trends in various Dy^{3+} doped glasses.

Sample	Ω_2	Ω_4	Ω_6	Trend
AEBTDy1.0 [1]	497	296	157	$\Omega_2 > \Omega_4 > \Omega_6$
G2 glass [2]	1725	462	460	$\Omega_2 > \Omega_4 > \Omega_6$
BPB0.5D [3]	699	200	144	$\Omega_2 > \Omega_4 > \Omega_6$
TZKCDy05 [4]	494	153	106	$\Omega_2 > \Omega_4 > \Omega_6$
TBZnD [5]	107	43	15	$\Omega_2 > \Omega_4 > \Omega_6$
LBGS-0.5Dy [6]	832	214	275	$\Omega_2 > \Omega_6 > \Omega_4$
BGGD1.00 [7]	365	65	157	$\Omega_2 > \Omega_6 > \Omega_4$
Dy:BaAS [8]	753	50	115	$\Omega_2 > \Omega_6 > \Omega_4$
TBZDy0.5 [9]	1432	564	264	$\Omega_2 > \Omega_4 > \Omega_6$

Table.1 represents the Judd-Ofelt (J-O) intensity parameters and their trend of various Dy^{3+} doped glasses [1-9] which were derived from the absorption spectra of the glasses that are mentioned in Figure.1. The intensity parameters share the information about structural environment and bonding around Dy^{3+} ions. The Ω_2 features the bonding nature of ligand and Dy^{3+} ion. Here, all the selected glasses have the larger Ω_2 values compared to other two Ω_4 and Ω_6. This domination of Ω_2 over Ω_4 and Ω_6 reveals the covalent nature of the ligand and Dy^{3+} ion bond as well as low symmetry around Dy^{3+} ion sites. The obtained Ω_2 values reveal that the selected glasses have low symmetry around the Dy^{3+} ions and covalent bond between Dy^{3+} ion and oxygen.The important optical properties such as stimulated emission cross-section (σ_{se}), gain band width (σ_{se} x $\Delta\lambda_p$), optical gain (σ_{se} x τ_R), experimental lifetimes (τ_{exp}), radiative lifetimes (τ_R), quantum efficiencies (η), non-radiative relaxation rates (W_{NR}) of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ level and CIE Chromaticity coordinates (X and Y), Y/B ratios of selected Dy^{3+} doped glasses are presented in Table.2 [1,3,5-12]. The emission spectra, Decay spectra and the colour coordinate diagrams of the selected glass systems are represented in Figure.2, Figure.3 and Figure.4 respectively. The white light emission capability of Dy^{3+} doped glasses can be related to few important optical parameters such as chromaticity coordinates (X, Y), Y/B ratios, quantum efficiency

TABLE 2
Stimulated emission cross-section (σ_{se}) (10^{-22} cm^2), gain band width (σ_{se} x $\Delta\lambda_p$) (10^{-28} cm^3), optical gain (σ_{se} x τ_R) ($10^{-25}$$cm^2$ s), experimental lifetimes (τ_{exp}) (µs), radiative lifetimes (τ_R) (µs), quantum efficiencies (η) (%), non-radiative relaxation rates (W_{NR}) (s^{-1}) of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ level and CIE Chromaticity coordinates (X and Y), Y/B ratios of various Dy^{3+} doped glasses.

Sample	σ_{se}	σ_{se}x$\Delta\lambda_p$	σ_{se}xτ_R	τ_{exp}	τ_R
AEBTDy1.0 [1]	36.59	58.23	10.50	245	287
BPB0.5D [3]	55.00	41.69	36.63	403	666
TBZnD [5]	5.55	40.74	14.70	414	3819
LBGS-0.5Dy [6]	48.26	-	-	573	773
BGGD1.00 [7]	20.93	40.83	17.62	386	842
Dy:BaAS [8]	24.20	-	-	834	912
TBZDy0.5 [9]	67.25	-	-	732	1060
Glass B [10]	28.70	51.10	6.41	155	168
BPA0.5D [11]	69.50	46.25	49.90	757	919
BiNFB0.5D [12]	44.91	35.04	41.55	445	925

Sample	η	W_{NR}	X	Y	Y/B ratio
AEBTDy1.0 [1]	85	597	0.362	0.387	3.20
BPB0.5D [3]	61	979	0.400	0.420	1.79
TBZnD [5]	15	3079	0.330	0.390	1.41
LBGS-0.5Dy [6]	-	-	0.410	0.420	1.70
BGGD1.00 [7]	46	1405	0.384	0.419	2.27
Dy:BaAS [8]	91	-	0.400	0.440	2.38
TBZDy0.5 [9]	69	3.56	0.430	0.440	3.70
Glass B [10]	92	475	0.294	0.348	0.71
BPA0.5D [11]	82	232	0.420	0.440	2.57

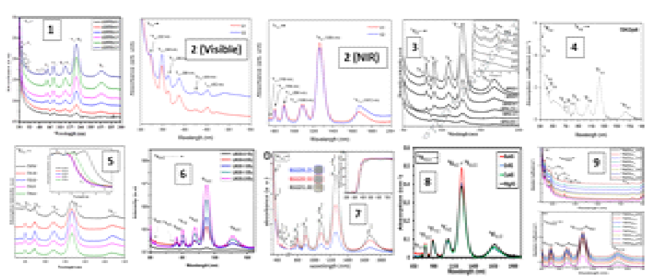
***Figure.1**: Absorption spectra of the glasses that are mentioned in Table.1*

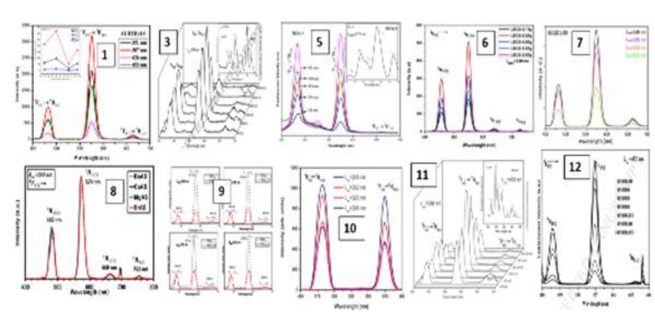
***Figure.2** : Emission spectra of glasses that are mentioned in Table.2*

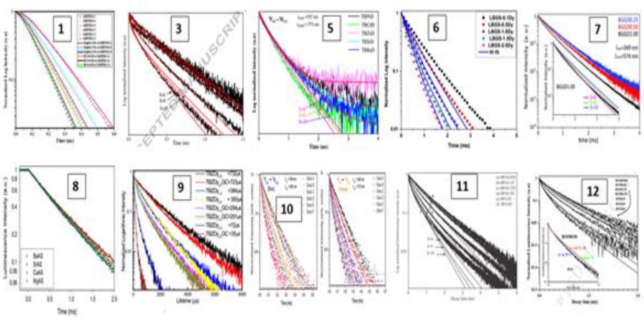

***Figure.3** : Decay spectra of glasses that are mentioned in Table.2*

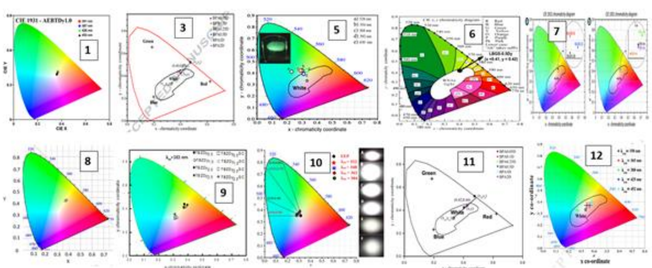

***Figure.4**: Colour coordinate diagrams of the glasses that are mentioned in Table.2*

and stimulated emission cross-section etc. For a good white light emitting material, the coordinates should be (0.333, 0.333). The higher magnitudes of Y/B ratios indicate lower symmetry around the Dy^{3+} ion sites and high covalency of the Dy-O bond. The higher values of stimulated emission cross-section and quantum efficiency indicate good lasing potentialities of the material. If we observe the Table.2, the Alkaline-Earth Boro tellurite glass AEBTDy1.0 of our previous study attained the colour coordinates as (0.362, 0.387), Y/B ratio as 3.20, σ_{se} as 36.59 x 10^{-22} cm^2 and η as 85%. Compared to other selected glasses such as BPB0.5D (Oxyfluoro-borophosphate glass), LBGS-0.5Dy (LBGS glass), BGGD1.00 (Gadolinium Borogermanate glass), Dy:BaAS (Alkaline-Earth Aluminosilicate glass), TBZDy0.5 (Zinc Borotellurite glass), BPA0.5D (Aluminofluoroborophosphate glass) and BiNFB0.5D (Bismuth Sodiumfluoroborate glass), the AEBTDy1.0 glass has better colour coordinates that are nearer to standard coordinates (0.333, 0.333) and the same glass has lower stimulated emission cross-section value compared to BPB0.5D (Oxyfluoro-borophosphate glass), LBGS-0.5Dy (LBGS glass), TBZDy0.5 (Zinc Borotellurite glass), BPA0.5D (Aluminofluoroborophosphate glass) and BiNFB0.5D (Bismuth Sodiumfluoroborate glass). If we keenly observe the Table.2, the glasses with colour coordinates of X > 0.4 and Y > 0.4 have higher σ_{se} values and the glasses with colour coordinates of X < 0.4 and Y < 0.4 have lesser σ_{se} values. So, from this trend of selected glasses, the stimulated emission cross-section and the colour coordinates of the selected glasses are inversely proportional. Since, the higher value σ_{se} gives the better lasing potentialities to the material, we can draw a conclusion that the glasses may yield better white light emission with low lasing potentialities i.e. low σ_{se} values.

4 CONCLUSIONS

Hence, various reported Dy^{3+} doped glasses were analyzed using their optical properties to understand their white light emission behavior. The glasses taken for analysis displayed low symmetry around Dy^{3+} ion and covalent nature for Dy^{3+}-O bond. The glasses with colour coordinates of X and Y > 0.4 have larger σ_{se} values and the glasses with colour coordinates of X and Y < 0.4 have lesser σ_{se} values. Thus, from the trend of (X, Y) coordinates and σ_{se} values of the selected glasses, we may conclude that the both parameters are inversely proportional and the glasses with less σ_{se} values may emit pure white light.

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