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Original Article

Optical Properties and White Light Emission of Dy^{3+}Doped Alumino Boro-tellurite Glasses

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Abstract: Dy^{3+}doped alumino boro-tellurite (ABT) glasses xB_2O_3+(80-x)TeO_2+10Al_2O_3+10CaO+ 0.5Dy_2O_3 (where x = 35; 45 and 55) have been prepared by melting method. Their optical properties were studied through absorption, luminescence spectra and decay time measurements. Judd-Ofelt (JO) intensity parameters (Ω_λ, λ = 2, 4 and 6) were determined using absorption spectra and were used to calculate the radiative parameters like transition probability, stimulated emission cross-section, branching ratios, gain band width and optical gain for the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition in Dy^{3+} ions. The chromaticity coordinates were used to estimate the emission feature of prepared glasses.

Keywords: Alumino boro-tellurite, Judd-Ofelt theory.

I. Introduction

Recently, white light emitting diodes (W-LEDs) are becoming as an interesting topic for scientists to study novel white light sources for its wide application purpose in lighting technology. Consequently a lot of importance is given for generation of white light in the different glasses and crystals by incorporating rare earth ions and transition metal ions [1, 2]. Among various rare earth (RE) ions, Dy^{3+} ion has attracted considerable and increased attention because it can alone emit near-white luminescence [2-4]. Dy^{3+} ions-doped crystals and glasses have been extensively studied due to its primary intense blue (484 nm, $^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow (575 nm, $^4F_{9/2} \rightarrow {}^6H_{13/2}$) emissions and an appropriate combination of these blue and yellow luminescence bands leads to generation of white light in the matrix [3-7]. These Dy^{3+}-doped solid state systems can be quite easily excited by the

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commercial UV or blue LEDs, because their excitation spectra exhibit several 4*f*-4*f* electronic bands in the 340-480 nm spectral range [6, 7]. Furthermore, it is widely known, the basic features of Dy^{3+} ions in crystalline and amorphous host matrices are so well established that these rare earth ions are extensively used as a spectroscopic probe for studying the structures and local symmetry of the solid state materials [7].

Borate based glasses have been studied extensively due to their special physical properties like excellent heat stability and lower melting temperature compared with other glasses [7-9]. The borate glasses were added with TeO_2, they can result in significant reduction in the phonon energy [7, 9]. This can increase the fluorescence efficiency of materials. In this paper, the optical properties of Dy^{3+} ions in alumino telluroborate glasses have studied using Judd-Ofelt (JO) theory [11, 12] and the CIE 1931 chromaticity diagram. The results have shown that alumino borotellurite glasses doped with Dy^{3+} ions are promising for optical applications and white light emission.

2. Experiments

The ATB glasses with the composition of $x B_2O_3+(80-x)TeO_2+10Al_2O_3+10CaO+0.5Dy_2O_3$ (where x = 35; 45 and 55, denoted by ABT35; ABT45 and ATB55, respectively) were prepared by conventional melt quenching. All the above weighed chemicals were well-mixed and heated for 120 min in a platinum crucible at 1300 ^oC in an electric furnace, then cooled quickly to room temperature. The ATB glasses were annealed at 350 ^oC for 12 h to eliminate mechanical and thermal stress. The optical absorption spectra were obtained between wavelengths 300 and 2000 nm using Jasco V670 spectrometer. The emission spectra were recorded by Fluorolog-3 spectrometer, model FL3-22, Horiba Jobin Yvon. Luminescence lifetime was measured using a Varian Cary Eclipse Fluorescence Spectrophotometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption spectra and intensity parameters

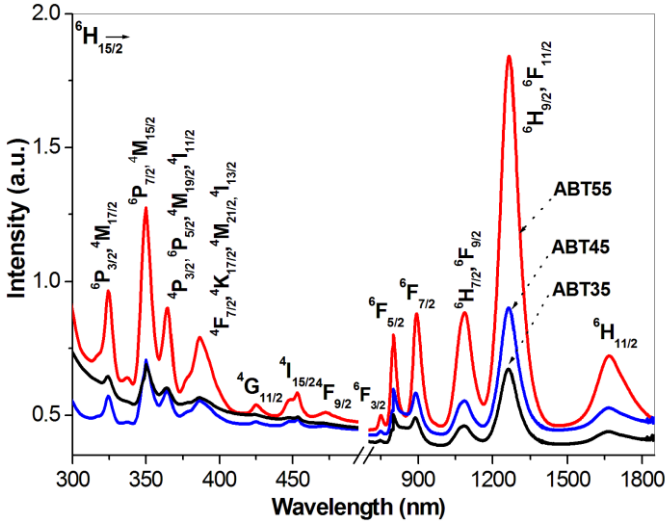

Fig. 1. Room temperature absorption of ABT:Dy^{3+} glasses.

Absorption spectra of Dy^{3+}-doped ABT glass are showed in Fig. 1. There are 13 absorption bands appearing at the wavelengths of 1667, 1266, 1081, 895, 801, 743, 473, 453, 425, 386, 365, 349 and 323 nm. These are the characteristic wavelengths in the absorption spectra of Dy^{3+} ions, which are attributed to transitions from the $^6H_{5/2}$ ground state to excited levels $^6H_{11/2}$, $^6H_{9/2}$+$^6F_{11/2}$, $^6H_{7/2}$+$^6F_{9/2}$ and $^6P_{3/2,5/2}$+$^4M_{19/2}$ $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^4F_{9/2}$, $^4I_{15/2}$, $^4F_{7/2}$+$^4K_{17/2}$+$^4M_{21/2}$+$^4I_{13/2}$,$^4P_{3/2}$+$^6P_{5/2}$+ $^4M_{19/2}$+$^4I_{11/2}$, $^6P_{7//2}$+$^4M_{15/2}$ and $^6P_{3/2}$+ $^4M_{17/2}$, respectively [13]. In NIR region, the transitions from $^6H_{15/2}$ to ^6H_J and ^6F_J are allowed by the spin selection rule ($\Delta S = 0$), so the intensity of these transitions is often quite strong. The $^6H_{15/2}\rightarrow{}^6F_{11/2}$ transitions obeys the selection rule of $|\Delta J| \leq 2$, $|\Delta S| = 0$ and $|\Delta L| \leq 2$, thus this is hypersensitive transitions [6, 7]. Usually, the position, shape and intensity of hypersensitive transitions in RE^{3+} ions are very sensitive to the ligand coordination [8, 9].

The Judd-Ofelt (JO) theory [11, 12] is seen to be useful to evaluate the radiative parameters of RE^{3+}-doped solids, as well as RE-doped aqueous solutions. According to the JO theory, the electric dipole oscillator strength of a transition from the ground state to an excited state is given by:

$$f_{cal} = \frac{8\pi^2 mc\nu}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda \left\| U^{(\lambda)} \right\|^2 \quad (1)$$

where n is the refractive index of the material, J is the total angular momentum of the ground state, Ω_λ are the JO intensity parameters and $\left\| U^{(\lambda)} \right\|^2$ are the squared doubly reduced matrix of the unit tensor operator of the rank λ = 2, 4, 6, which are calculated from intermediate coupling approximation for a transition $|\Psi J\rangle \rightarrow |\Psi' J'\rangle$. These reduced matrix elements are nearly independent of host matrix as mentioned in earlier studies [11].

On the other hand, the experimental oscillator strengths, f_{exp}, of the absorption bands are experimentally determined using the following formula [7, 8]:

$$f_{exp} = 4.318 \times 10^{-9} \int \alpha(\nu) d\nu \quad (2)$$

where α is molar extinction coefficient at energy ν (cm^{-1}) = $10^7/\lambda$ (nm). The $\alpha(\nu)$ values can be calculated from absorbance A by using Lambert–Beer's law

$$A = \alpha(\nu) cd \quad (3)$$

where c is RE^{3+}concentration and d is the optical path length.

By equating the measured and calculated values of the oscillator strength (f_{cal} and f_{exxp}) and solving the system of equations by the method of least squares, the JO intensities parameters Ω_λ (λ = 2,4 and 6) can be evaluated numerically. The calculated results Ω_λ for ABT:Dy^{3+} glasses are shown in Table 1.

Table 1. The intensity parameters Ω_λ (10^{-20} cm^2) of ABT:Dy^{3+} glasses.

Samples	Ω_2	Ω_4	Ω_6
ABT35	14.05	3.59	5.03
ABT45	14.43	2.43	4.47
ABT55	14.98	4.69	6.32

3.2. Emission spectra and color coordinates

Fig. 4 illustrates the measured emission spectra using the 450 nm excitation wavelength of xenon lamp source. Four emission bands at 481, 575, 665 and 755 nm which are attributed to transitions from

4F9/2 to 6H15/2, 6H13/2, 6H11/2 and 6H9/2+6F11/2 states, respectively [13]. Among of them, the yellow (Y) band (575 nm) corresponds to the hypersensitive transition 4F9/2→6H13/2, (ΔL = 2, ΔJ = 2) and the blue (B) band (481 nm) corresponds to the 4F9/2→6H15/2 transition are the dominant bands in the emission spectrum [7, 15]. The Y- band is hypersensitive and its intensity strongly depends on the host, in contrast to less sensitive B-band, therefore the Y/B ratio is strongly changed with the glass compositions [15, 16]. The higher values of Y/B indicate the higher distortion of site symmetry and the higher degree of covalence between Dy3+ and oxygen ions. With this specific feature, the Dy3+ ion is one of two best rare earth ions (another one is Eu3+ ion) used as the optical probe to study relation between glass composition, bonding nature and local symmetry in its surrounding. The Y/B ratios of the ABT:Dy3+ glass samples are calculated and presented in Table 2. It is seen that the Y/B ratios of ABT:Dy3+ glasses are larger than unity for all samples, i.e. the yellow emission is dominant in ABT:Dy3+ glasses. This shows that the environment around Dy3+ ions has the low symmetry without inversion center [16].

Table 2. Y/B ratios and color coordinates (x, y) of ABT:Dy^{3+} glasses

Samples	Y/B	x	y
ABT35	1.32	0.352	0.385
ABT45	1.51	0.332	0.375
ABT55	1.22	0314	0.358

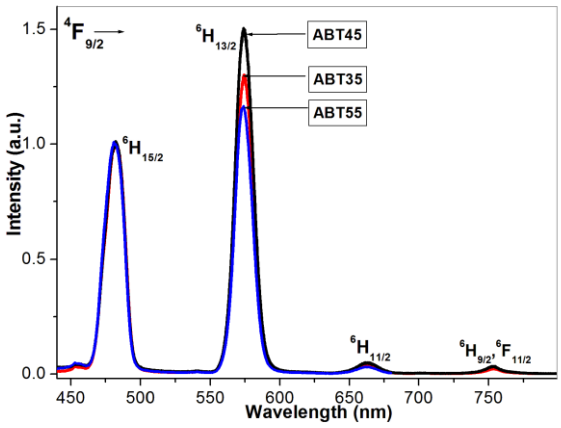

Fig. 2. Emission spectra (λ_{ex} = 450 nm) of the glasses with different B_2O_3/TeO_2 ratios.

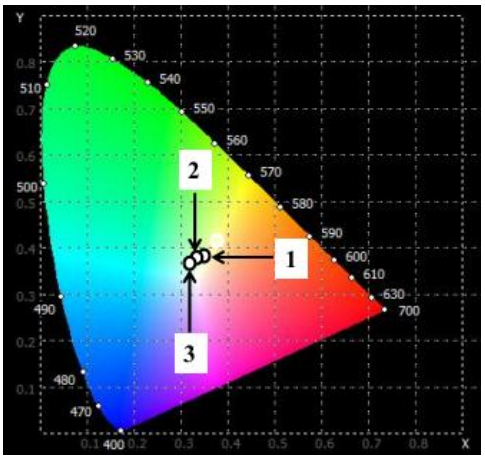

Fig. 3. CIE chromatic coordinates diagram: (1) ABT35, (2) ABT45 and (3) ABT55 glasses.

The (Y/B) ratio is especially interested for lighting technology. The line linking the yellow and blue wavelengths in the CIE 1931 chromaticity diagram usually passes through the white light region. Therefore, by adjusting to a suitable Y/B ratio, the chromaticity coordinates of the phosphors containing Dy^{3+} can be adjusted to the white light zone and these phosphors could be used suitably for the white-lighting. The generation of white light of the system has been excited by wavelength 450 nm and analyzed in the frame work of the chromaticity color coordinates theory is also presented in Table 2 and Figure 3. In the present work, for all three studied samples, the color coordinates are located

near the center of chromaticity diagram. This result indicates that the present glasses may be used for white light generation with the excitation of blue light (450 nm).

3.3. Radiative properties of Dy^{3+} ion in ABT glasses

It is noted that the luminescence branching ratio characterizes the possibility of attaining stimulated emission from any specific transition, so it is a critical parameter to the laser designer and other optical applications [6, 16, 17, 18]. Vijaya [16] and Mahamuda [17] reported that if the branching ratio of an emission transition is greater than 50 %, this transition is potentiality for laser emission. For ABT:Dy^{3+} glasses, the measured branching ratios of the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition are 55.6, 59.2 and 51.4 for ABT35, ABT45 and ABT55 samples, respectively. So, the radiative parameters of this transition such as effective line width ($\Delta\lambda_{eff}$), stimulated emission cross-sections ($\sigma_{\lambda p}$), calculated (τ_R, μs), experiment (τ_{exp}, μs) lifetime, quantum efficiency (η, %), gain band width ($\sigma_{\lambda p}\times\Delta\lambda_{eff}$) and optical gain ($\sigma_{\lambda p}\times\tau_R$) have been calculated for all samples. The details of this theory were shown in previous reports [7, 14, 15]. The results (Table 3) show that the radiative parameters of the ABT45 are the largest of all. These values are higher than those in some other glasses [5, 6, 8, 16, 17]. Thus, ABT:Dy^{3+} glasses are found to be suitable for developing the yellow laser and fiber optic amplifier.

Table 3. Radiative properties: ($\Delta\lambda_{eff}$, nm), ($\sigma(\lambda_P)$, 10^{-22} cm^2), ($\Sigma_{JJ'}$,10^{-18} cm), (β_{exp}, %), ($\sigma(\lambda_P)\times\Delta\lambda_{eff}$,$10^{-28}$ m^3), ($\sigma(\lambda_P)\times\tau_R$, 10^{-25} cm^2s) of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition and calculated (τ_R, μs), experiment (τ_{exp}, μs) lifetime, quantum efficiency (η, %) of Dy^{3+} ion.

Sample	$\Delta\lambda_{eff}$	$\sigma(\lambda_P)$	$\Sigma_{JJ'}$	β_{exp}	τ_R	τ_{exp}	$\sigma\times\Delta\lambda$	$\sigma\times\tau_R$	η (%)
ABT35	16,40	52,92	2,56	53,76	512	440	86,71	24,41	85.9
ABT45	16,50	59,12	2,45	58,46	494	432	97,54	26,75	87.4
ABT55	16,13	58,72	2,85	50,98	487	412	94,17	25,25	84.6

3.4. Luminescence decay

The measured fluorescence decay curves at 575 nm corresponding to $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition for all samples are shown in Fig. 4. Experimental lifetimes ($\boldsymbol{\tau}_{exp}$) of samples have been determined by [7, 14, 18]:

$$\tau_{exp} = \frac{\int tI(t)dt}{\int I(t)dt} \quad (4)$$

The experimental lifetime of $^4F_{9/2}$ is found to be 440, 432 and 412 μs for the ABT35, ABT45 and ABT55, respectively. It is seen that the experimental lifetime τ_{exp} is smaller than calculated lifetime τ_R. Additionally, the lifetime decreases with increasing of B_2O_3 concentration in glass matrix. The discrepancy between the measured and calculated lifetime can relate to nonradiative processes including of multiphonon relaxation and energy transfer through cross-relaxation between Dy^{3+} ions [6, 7,15, 16].The fluorescence quantum efficiency η is defined as the ratio of the number of photon emitted to the number photon absorbed. For this case, it is equal to the ratio of the experimental lifetime to the predicted lifetime for the $^4F_{9/2}$ level and it is given by [7, 14, 18]:

$$\eta(\%) = \frac{\tau_{exp}}{\tau_R}\times 100\% \quad (8)$$

The results are presented in Table 2. It is found that the quantum efficiency of the ABT45 sample is the highest of all and achieves 87.4 %. This is suggested that Dy^{3+}:ATB45 glass is a potential material for 575 nm yellow laser applications.

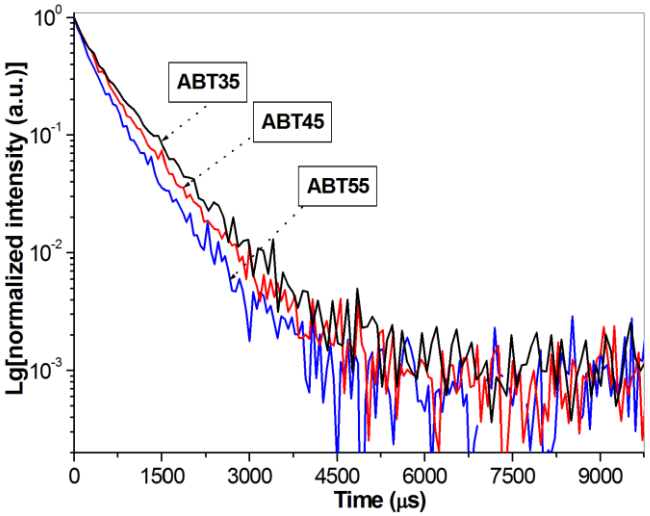

Fig. 5. Luminescence decay profiles of the $^4F_{9/2}$ level in Dy^{3+} ions doped ABT glasses.

4. Conclusion

The optical properties of Dy^{3+}-doped alumino borotellurite glasses have been investigated. By using JO theory, the radiative properties such as branching ratios and the stimulated emission cross-section have been predicted. The large values of the branching ratios, the stimulated emission cross-section and quantum efficiency show that ABT:Dy^{3+} glass is the promising materials for lasing action and optical amplifier through the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission transition. Despite of the complicated relation between Y/B emission ratios of the Dy^{3+} and the host compositions, all the prepared samples present the visible emission spectra with chromaticity coordinates in the white light region under excitation by 365 nm. They have potential application for white LED technology.

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