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Optical Properties of Dy^{3+} Doped Boro-tellurite Glasses

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Abstract: Dy^{3+}-doped glasses with various compositions $(30+x)B_2O_3$+ $(60-x)TeO_2$ + $9Na_2O$ + $1Dy_2O_3$ (x = 10 and 20) were prepared by a melt–quenching technique. The specifically structural properties of boro-tellurite glasses with the high borate content (> 30 mol%) was reflected in the unusually large values of the Judd-Ofelt parameters Ω_2 and Ω_6 . The CIE chromaticity color coordinates were calculated from the luminescence spectra of Dy^{3+} ions of the glasses with the different compositions and all of them were located in the white light zone of the color coordination diagram.

Keywords: Boro-tellurite, Dy^{3+}, white light.

1. Introduction

Nowadays, white light emitting diodes (W-LEDs) are becoming an interesting topic for scientists with the goal of finding novel white light sources for its wide application purpose in lighting technology. Among various rare earth (RE) ions, Dy^{3+} ion has attracted considerable and increased attention because it can alone emit near-white luminescence. Dy^{3+}ions-doped crystals [1,2] and glasses [3,4] 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.

The main objectives of the present study are following:

1. To study the relation between the structure and optical properties of the Dy^{3+} doped boro-tellurite glasses with the emphasis on the glasses having high borate content (> 30 mol%).

2. Estimating the possibilities to use the Dy^{3+} doped boro-tellurite glasses as a potential material for generating white light.

2. Experimental

Dy^{3+}-doped boro-tellurite glasses were prepared from the starting materials of B_2O_3, TeO_2, Na_2O and Dy_2O_3 with the following molar compositions $(30+x)B_2O_3$+ $(60-x)TeO_2$ + $9Na_2O$ + $1Dy_2O_3$ (x = 10 and 20), which were named by S10 and S20, respectively.

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The mixed powder was grinded in an agate mortar and melted in platinum crucible using an electric furnace at 1100-1200 °C for 1 h so that a homogeneous melt was obtained.

The obtained glass samples were subsequently annealed at 400 °C for 6 h, after that they were slowly cooled down to room temperature. This annealing process was made to avoid the undesirable thermal strain. For optical measurements, the glass samples were sliced and polished to get a uniform thickness of 2 mm.

Absorption spectra were carried out using Cary 5E (Varian Instruments, Sugar lane, Tex) in the wavelength region 200-2500 nm with a spectra resolution of 1.0 nm. The emission and excitation spectra were recorded in a Fluorog 3-22 (Horiba Jobin-Yvon) with 450 W Xe lamp at room temperature. Refractive index for these glasses was measured by an Abbe's refractometer at sodium wavelength. All the measurements were performed at room temperature.

An in depth Judd-Ofelt analysis was used to clarify some specific optical properties of Dy^{3+} ion of this glass.

3. Results and discussion

3.1. X-ray diffraction data

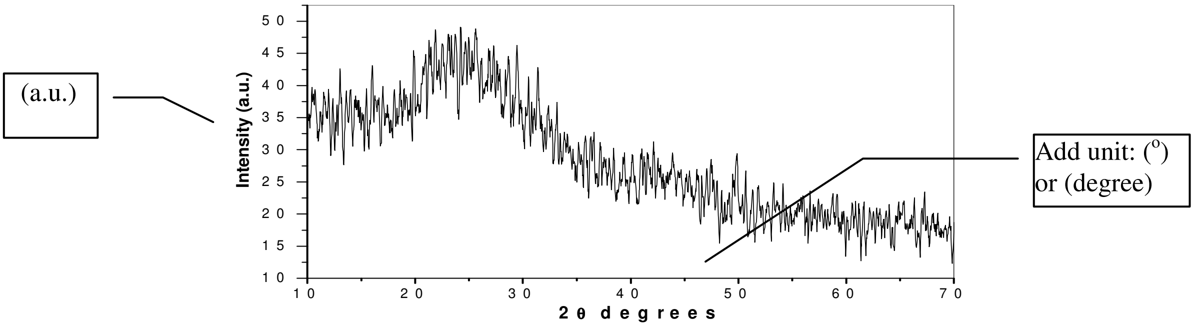

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Fig.1. The XRD pattern of the sample S10

The small concentration of Dy^{3+}ions (1mol%) is doped for all samples in order to reduce the concentration quenching effect. The XRD pattern of the sample S10 shown in Fig.1 as a representative case exhibits a broad scattering at low angle suggesting the amorphous nature of present boro-tellurite glasses.

3.2. Absorption spectra and Judd-Ofelt analysis

Absorption spectra of the sample S10 in two regions of wavelength 250–400 nm and 700–1800 nm are showed in Fig. 2. The spectra of the other samples exhibited similar characteristic features with slight change in the intensities of various absorption bands. The nine of observed absorption bands were assigned to different transitions from the $^6H_{15/2}$ ground state to the exited states of $4f^9$ electronic configuration of Dy^{3+} ions by comparing the peak positions with those reported previously [4].

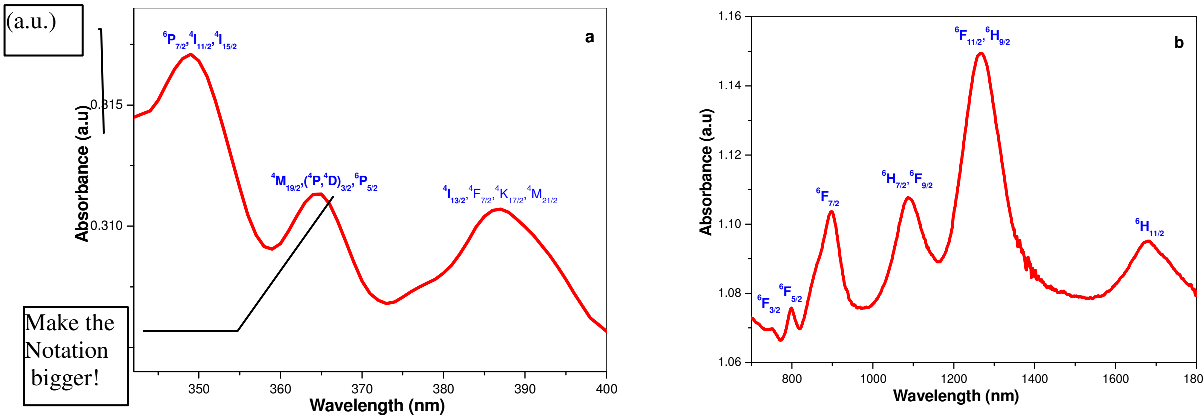

Fig. 2. Absorption spectra of S10:Dy glass in UV (a) and NIR regions (b).

It is noted that in the UV-region, the absorption bands overlap and the assignments to each separated transition cannot be made easily due to the dense energy level scheme of Dy^{3+} ions. Besides, the absorption bands in the NIR wavelength range have stronger intensities because these transitions satisfy well the spin selection rule.

The determination of intensity parameters for Dy^{3+} has inherent difficulties due to the lying close to each other of a large number of energy levels. In this case, we can take advantage of the property that both the dipole strengths and the squared reduced matrix elements of overlapping transitions are additive. For the transitions overlap, it is necessary to integrate all the transitions contribution to one absorption band together. The corresponding reduced matrix elements have to be summed (for example, the additive technique was used for overlapped bands $^6H_{15/2}\rightarrow{}^6F_{5/2} + {}^6F_{3/2}$, $^6H_{15/2}\rightarrow{}^6F_{9/2} + {}^6H_{7/2}$, $^6H_{15/2}\rightarrow{}^6F_{11/2} + {}^6H_{9/2}$ ...).

In this study, we would like to calculate the Judd-Ofelt parameters and to clarify the relations between these Ω_λ values and the increase of disorder, the reduction of the rigidity of boro-tellurite glasses compared with that of single borate or tellurite glass.

Table 1. The J-O intensity parameters Ω_λ ($\times10^{-20}$ cm^2) of boro-tellurite glasses S10, S20 and other oxide glasses containing either tellurite or borate component.

Sample	Ω_2 ($\times10^{-20}$ cm^2)	Ω_4 ($\times10^{-20}$ cm^2)	Ω_6 ($\times10^{-20}$ cm^2)	Refs.
S10	13.26 ± 0.98	2,34 ± 0.76	4.01 ± 0.83	This work
S20	12.78 ± 1.32	4,24 ± 0.67	5.85 ± 0.65	This work
ZnPbNaTe:1Dy	5.66	0.84	2.17	[5]
TiWTe:0.5Dy	3.13	0.29	0.97	[6]
PbWTe:0.5Dy	5.19	1.93	1.07	[7]
BiZnB:0.5Dy	4.73	0.63	1.99	[8]
NaCaB:0.5Dy	6.30	0.35	2.30	[9]
PbZnLiB:1Dy	5.70	2.0	1.24	[10]

Table 1 shows that the calculated values of Ω_2 and Ω_6 for the boro-tellurite glass samples are much larger than that of the other tellurite or borate glasses. It is known that values of Ω_2 and Ω_6 parameter are related not only to peculiarities of the fitting procedure, but they have also the strongly relation to the physicochemical characteristics of the system studied. Our most attention has been paid to the B_2O_3/TeO_2 compositional dependence of the Ω_λ parameters in the boro-tellurite glasses.

From the FTIR and X-ray diffraction studies [11,12], it is well-known that the framework of binary boro-tellurite glasses is built up of $[BO_4]$ tetrahedral, $[BO_3]$ triangles, trigonalbipiramids $[TeO_4]$, pyramidal $[TeO_3]$ and accidently $[TeO_6]$ octahedral or/and $[TeO_5]$ groups at high B_2O_3 content (>30%). The number of oxygen of TeO_n polyhedra relates closely to the $[BO_4]$ tetrahedral structures. Such it is different from majority of the glassy oxides, in two-component TeO_2 glasses the Te ions are assigned a co-ordination number of six and correspondingly in the tellurite glasses there are greatly deformed $[TeO_6]$ octahedra and the short-range order should not be tetrahedral [12,13]. S.Rada [14] reported that when increasing the B_2O_3 content, the ratio of tetrahedral $[BO_4]$ to trigonal $[BO_3]$ units is changed. The increase in the number of non-bridging oxygen atoms would decrease the connectivity of the glass network, resulting in a depolymerization of borate chains and a radical rearrangement of the network formed by $[TeO_6]$ octaheda. Brady [12] suggested that an addition of B_2O_3 reduces the rigidity of structure and easily produces the high disorder of BTe-glass. Bobovich [15] reported that a high B_2O_3 content (30%) causes a rearrangement of network formed by the $[TeO_6]$ octahedral and creates the breakdown of the edges bonds of these $[TeO_6]$ octahedra.

It is well-known, the main reasons for the large Ω_2 values are the high degree of covalence between Dy^{3+} and oxygen ions and the low symmetry (or the high disorder) of the coordination structure surrounding the Dy^{3+} ion. The later is related directly with the B/Te content ratio. When the B/Te ratio increases, the coordination sphere around Dy^{3+} is changed to the higher disorder due to more non-bridging oxygen ions and existence of the $BO_4 \rightarrow BO_3$ conversion.

The Ω_6 parameter is related to the rigidity of the medium in which the lanthanide ions are embedded. Rigid matrices show low values for the Ω_6 parameter. In the present material, the large values of Ω_6 parameter for the B/Te glasses compared with those of the tellurite (without borate) or borate (without tellurite) glasses as shown in Table 1 could be explained by the reducing rigidity of these glasses. The reduction of the rigidity is due to the rearrangement of network formed by the $[TeO_6]$ octahedra and creates the breakdown of the edges bonds of these $[TeO_6]$ octahedra when the borate content of the boro-tellurite glasses increases.

3.3. White light emission

It should be pointed out in [16] that the intensity ratio of yellow emission – blue emission (Y/B) should increase when the Ω_2 value increase [16,17,18], according to the following equation:

$$\frac{Y}{B} \propto \frac{0.051\Omega_2 + 0.0172\Omega_4 + 0.0573\Omega_6}{0.00\Omega_2 + 0.0049\Omega_4 + 0.0303\Omega_6}$$

consequently, this ratio is influenced by site asymmetries and electro-negativities of the ligand ions [19,20]. This relation could be used to adjust the value of Y/B ratios by changing the host composition.

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. From the emission spectra of the BxTey:Dy^{3+} samples (Fig. 3a) the integrated intensity ratios of yellow to blue (Y/B) are calculated and presented in Table 2. The changing of these ratios is originated from the changing in the environment of Dy^{3+} ions in glasses as it involves a hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$, ($\Delta L$= 2, ΔJ= 2), but generally, this ratio depends also on the excitation wavelength [21].

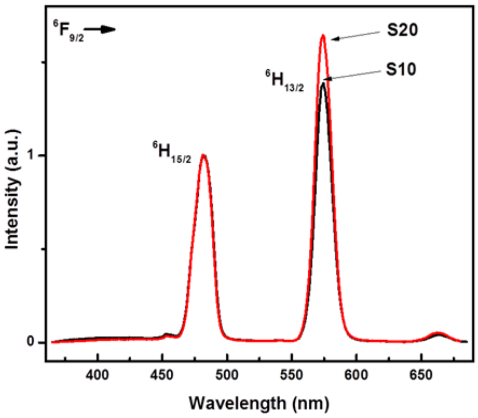

Fig. 3a. The normalized luminescence spectra (λ_{ex}= 450 nm) of the sample S10 and S20.

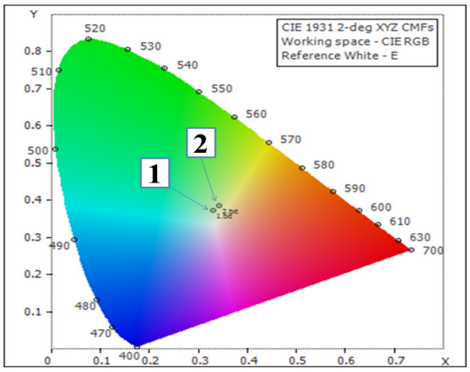

Fig. 3b. The calculated color coordinations of the sample S10 and S20 are presented in chromatic coordination diagram.

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, which is presented Fig.3a, b and Table 2. In our researches on Dy^{3+} ion doped boro-tellurite glasses, all studied samples present the color coordinations in the white light zone of chromaticity diagram.

Table 2. The experimental Y/B ratios and the calculated CIE chromatic coordination of the sample S10 and S20

Samples	Y/B	(x,y)
S10	1.32	(0.32; 0.37)
S20	1.41	(0.34; 0.38)

The complicated dependence of the Y/B ratios on the sample composition could be originated from the drastically changes of the vibrational spectra on the B/Te ratios in the boro-tellurite glasses [14] and also from the large discrepancy between the calculated and experimental Y/B intensity ratios, which are observed in some Dy^{3+} doped compounds [16]. However, these results indicate that the present glasses may be used for white light generation with the excitation of blue light (450 nm).

4. Conclusion

The relationship between structural features and the compositions of boro-tellurite glasses doped with Dy^{3+} ion was studied by the Judd-Ofelt analysis.

The Judd-Ofelt analysis of Dy^{3+}- doped boro-tellurite glasses containing different borate contents showed the drastically large values of the Ω_2 and Ω_6 compared with those of the single borate or tellurite glasses. The obtained values of the J-O parameters Ω_2 and Ω_6 are in agreement with the unusual change of the disorder structure and the rigidity of the boro-tellurite glass containing the high content of borate. When the B/Te ratio increased, the coordination sphere around Dy^{3+} was changed to the higher disorder with more non-bridging oxygen ions and with the existence of the $BO_4 \rightarrow BO_3$ conversion, which leads to the increase of the Ω_2 value. In present report, the large values of Ω_6 for the B/Te glasses could be explained by the reducing rigidity of these glasses which originated from the creating of the disorted $[TeO_6]$ octahedra at the glasses containing the high content of the boric oxide.

Despite of the complicated relation between Y/B emission ratios of the Dy^{3+} and the host compositions, all the Dy^{3+} doped boro-tellurite glass samples present the visible emission spectra having chromaticity coordinates in the white light region under the excitation by 365 nm and 450 nm wavelength. They have potential application for white LED technology.

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