Optical spectral studies of Ce³⁺ and Tb³⁺ ions co-doped in alkali borate glasses

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Abstract — Spectroscopic properties of Tb³⁺ and Ce³⁺ ions doped alkali metal borate glasses $(70-x-y)B_2O_3.15Li_2CO_3.15Na_2CO_3.xTb_2O_3.yCeO_2$ (BLN:Ce,Tb) fabricated by melting method have been studied. The emission intensity of Ce³⁺ or Tb³⁺ in BLN:Ce or BLN:Tb glasses is influenced by the Ce³⁺ or Tb³⁺ doping content, and the optimum concentrations of Ce³⁺ and Tb³⁺ are 0.75 mol% and 0.5 mol%, respectively. The concentration quenching effect of Ce³⁺ or Tb³⁺ in BLN:Ce³⁺,Tb³⁺ glasses occurs, and the concentration quenching mechanism is d–d interaction for either Ce³⁺ or Tb³⁺. The BLN:Ce³⁺,Tb³⁺ glasses can produce color emission from blue to green by properly tuning the relative ratio between Ce³⁺ and Tb³⁺, and the emission intensity of Tb³⁺ in BLN:Ce³⁺,Tb³⁺ glasses can be enhanced by the energy transfer from Ce³⁺ to Tb³⁺. The results indicate that BLN:Ce³⁺,Tb³⁺ may be a promising double emission for white light emitting diodes.

Keywords: **Tb³⁺ and Ce³⁺ ions; alkali metal borate glass, the concentration quenching mechanism.**

I. INTRODUCTION

White light-emitting diodes (LEDs) offer many advantages such as long service lifetime, thermal resistance, and high efficiency [4,9,10,11]. Therefore, white LEDs are expected to be a new light source in the illumination field. Besides that, due to the unique structural and physicochemical properties, alkali metal borate glasses doped with RE ions have been widely used as laser materials, optical amplifiers, optical memories, optoelectronics and magneto-optical devices [3,4, 6]. The presence of structurally different borate units in alkali metal borate glasses is favorable for spectroscopic investigations of RE ions.

These structural differences are usually correlated to chemical composition, type of modifiers and conditions during glass preparation. Broad band emitters are usually used to sensitize the luminescence of rare earth and transition metal ions. Particularly, the Ce³⁺ ion shows an efficient broad band emission due to its 5d–4f electric dipole allowed transitions. Ce³⁺ ions act as a good sensitizer in co-doped materials, and transfer a part of their energy to activator ions such as Eu²⁺, Tb³⁺ or Mn²⁺ [4,7,12]. In most of the cases, this kind of energy transfer belongs to resonance type.

In recent years, the resonance energy transfer between impurity ions in a solid material has been the subject of intense research, mainly because of its importance in the development of efficient phosphor materials for solid state lighting. As an important family of luminescent materials, chloroborates have attracted much attention. Recently, Eu²⁺, Ce³⁺, or Ce³⁺/Eu²⁺ doped chloroborates were reported [13,14,15]. However, to the best of our knowledge, little attention has been paid to the luminescent properties of rare-earth co-doped in BLN glasses. Among the rare-earth ions, Ce³⁺ and Tb³⁺ ions are two of the most important luminescent centers. Therefore, in the present paper, the luminescent characteristics and the energy transfer from Ce³⁺ to Tb³⁺ in BLN glasses are investigated. The glasses can create the color emission from blue to green. They can be effectively excited by UV and near-UV, and are suitable for serving as white LEDs [4,11].

II. EXPERIMENTS

Alkali metal borate glass doped with Tb³⁺ or/and Ce³⁺ were prepared by conventional melt quenching technique. The stoichiometric ratio of BNL glasses is $(70-x-y)B_2O_3-15Na_2O-15Li_2O-xTb_2O_3-yCe_2O_3$. The metal oxides were weighed accurately in an electronic balance mixed thoroughly and ground to a fine powder. The batches were then placed in quartz cup and melted in an electrical furnace in air at 1323 K for 1.5 hours. The melt was quenched to room temperature in air. The glasses were then annealed at 650 K for 2 hours.

The glasses thus obtained were throughout, evenly, no bubble. The samples were cut, grinded, polished to form cylinder block shape with product size: thickness d = 0.1 mm, radius r = 6.0 mm (used for the measurement of refractive index n, density, absorption and fluorescence); crushing and sorting grab particles range in size from 76 to 150 micron powder products (used for X-ray diffraction). The glass formation was confirmed by powder X-ray diffraction.

The measurement of the refractive index n is performed on the system Abbe refractometer at a wavelength of Na lamp, 589 nm with $C_{10}H_7Br$ (1 - bromonaphthalin) used as the liquid in contact. The measurement of density made by Archimede method, using xylene as immersion liquid form. Optical absorption spectra were recorded in the wavelength regions 200 nm – 2500 nm using Varian spectrometer system Cary 5E UV-VIS-NIR, with a resolution of 1 nm. Fluorescence spectra were obtained at room temperature using Flourolog - 3 Model FL3 - 22, resolution of 0.3 nm, excitation light xenon (Vehicle).

III. RESULTS AND DISCUSSION

A. Spectrum properties of BLN: Ce^{3+} and $BLN:Tb^{3+}$ glasses

Figure 1 (a, b) shows the excitation and emission spectra of BLN: Ce^{3+} glasses and the crystal - field splitting of both the $4f^1$ ($^2F_{5/2}$, $^2F_{7/2}$) and $5d^1$ ($^2D_{3/2}$, $^2D_{5/2}$) electronic configurations of Ce^{3+} in D_{3h} symmetry. In Fig.1(a), the excitation spectrum of BLN: $0.5Ce^{3+}$ monitored at 410 nm shows a broad band extending from 220 nm to 400nm due to the 4f–5d transition of Ce^{3+} ions.
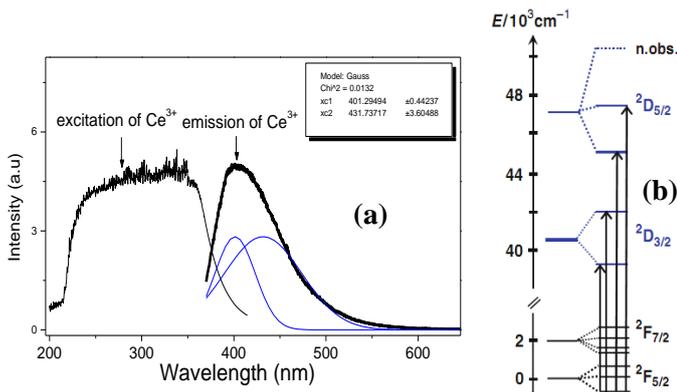

Fig 1. Emission and excition spectra of Ce^{3+}doped BLN glasses (a) and Assignment (D_{3h} symmetry) (b)

BLN: $0.5Ce^{3+}$ shows an asymmetric band extending from 350 nm to 670 nm with a maximum at about 410 nm under the 365 nm excitation. The characteristic double emission of Ce^{3+} ions is not clearly observed in the emission spectrum, but it can be resolved by a Gaussian fitting into two emission bands with the peaks at 401 nm (24933 cm^{-1}) and 431 nm (23201 cm^{-1}), respectively. However, the energy difference between the two fitted emission peaks is about 1732 cm^{-1}, which is smaller than that of the theoretically calculated value between $^2F_{5/2}$ and $^2F_{5/2}$ levels (2050 cm^{-1}). It means that there are two types of Ce^{3+} emitting centers in the phosphor due to different occupancies in the host BLN glasses, and the result is consistent with that in Ref. [2,4]. Broad band emission (violet luminescence) are characteristic of displacement 4f-5d. The 4f–5d transitions have high energies and only those of Ce^{3+}, Pr^{3+} and Tb^{3+} are commonly observed [1].

The crystal - field splitting of both the $4f^1$ ($^2F_{5/2}$, $^2F_{7/2}$) and $5d^1$ ($^2D_{3/2}$, $^2D_{5/2}$) electronic configurations of Ce^{3+} in D_{3h} symmetry in Fig 1b shows that the third transition to $^2D_{5/2}$ is not observed because it lies at too high energy. Conversely, the Ce^{3+} luminescence can be tuned from about 300 to 500 nm, depending on the matrix into which the metal ion is inserted due to large crystal - field effect on the $5d^1$ excited state [1,3].

Figure 2 depicts the excitation and emission spectra of BLN: Tb^{3+} glasses. The excitation spectrum exhibits a series of sharp peaks between 250 nm and 400 nm. The sharp bands between 280 nm and 400 nm are assigned to the intra $^4f_8$

transitions between the $^7F_6$ and $^5F_{5,4}$, $^5H_{7-4}$, $^5D_{1,0}$, $^5L_{10-6}$, $^5G_{6-2}$, and $^5D_{2-4}$ levels [4]. The emission spectrum of BLN: Tb^{3+} glasses excited by 365 nm presents four peaks at around 487 nm, 541 nm, 584 nm, and 621 nm which originate from the transitions between the excited $^5D_4$ level and ^7F_J (J=6,5,4,3) level of Tb^{3+} ion, respectively [1,4]. The strongest emission peak is located at 541 nm, corresponding to the typical transition $^5D_4-^7F_5$ of Tb^{3+} ion.
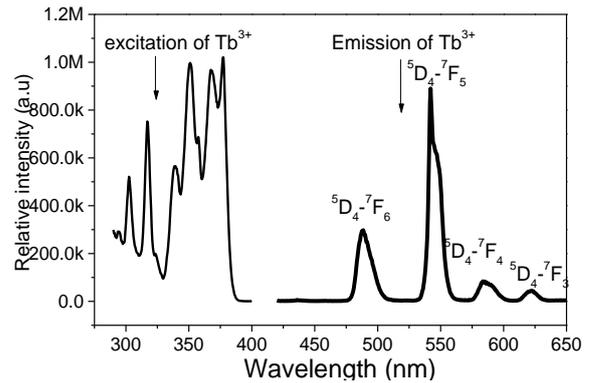

Fig 2. Emission and excition spectra of Tb^{3+}doped BLN glasses

B. Concentration quenching mechanism of Ce^{3+} or Tb^{3+} in BLN glasses
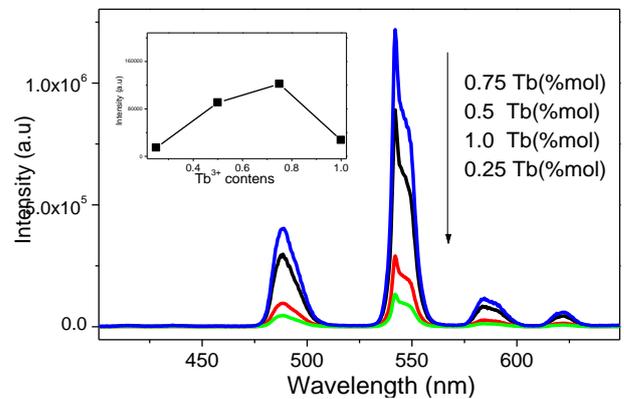
Fig 3. Emission spectra of BLN: xTb with several different values of Tb^{3+} content.

For BNL:Tb^{3+} glasses, the values of Tb^{3+} optimum doping content were discussed. The results are shown in Fig 3. The emission intensity first increases with the increasing of Tb^{3+} doping content, and reaches a maximum at 0.75 mol% Tb^{3+}, then decreases. For BLN:Ce^{3+}, the results are similar to those of BLN:Tb^{3+}, and shown in the Fig 4, and the maximal emission intensity is observed when Ce^{3+} doping content increases up to 0.5 mol% Ce^{3+}. The phenomenon of decrease in emission intensity after a certain concentration is called concentration quenching and attributed to energy migration among rare earth ions. As a representative, the concentration quenching mechanism of Tb^{3+} in BLN:Tb^{3+} were studied. Non - radiative energy transfer from one Tb^{3+} to another Tb^{3+}

ion may occur by exchange interaction, radiation re - absorption or multiple – multiple interaction: Tb^{3+} is an isolated emission centre in $BLN:Tb^{3+}$ [2,4,13]. The transition
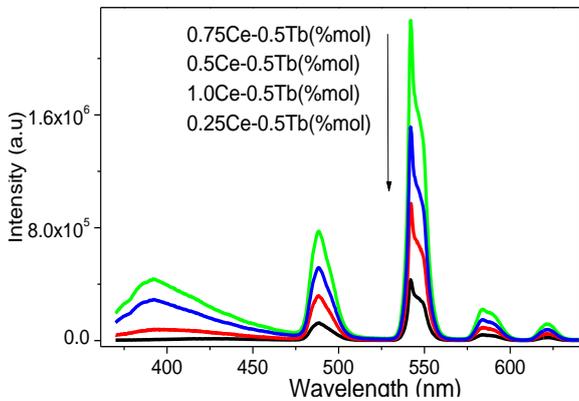

Fig 4. Emission spectra of BLN: xCe,0.5Tb with several different values of Ce^{3+} content.

of Tb^{3+} is allowed while exchange interaction is responsible for the energy for forbidden transitions. It means that the mechanism of exchange interaction plays no role in the energy transfer between Tb^{3+} ions in $BLN:Tb^{3+}$. The mechanism of radiation re - absorption comes into effect only when a broad overlap of the emission spectra of the sensitizer and activator appears, and in the view of spectrum properties of $BLN:Tb^{3+}$ the overlap is unlikely to happen. If the energy transfer occurs between the same sorts of activators, the multi - polar interaction can be determined from the change of the emission intensity [2,4].

C. Spectral properties of $BLN:Ce^{3+},Tb^{3+}$ glasses

Figure 5 exhibits the emission spectra of BLN: $0.5Ce^{3+}$, xTb^{3+}. With the increase of Tb^{3+} concentration, the phosphors can create color emission from blue to yellowish – green. Moreover, while the emission intensity of Ce^{3+} decreases dramatically and monotonically, the emission intensity of
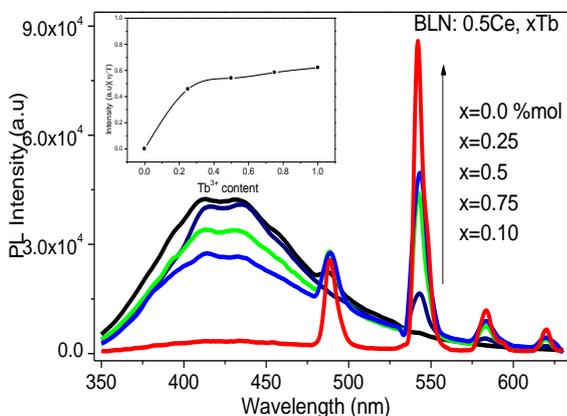

Fig 5. Emission spectra of BLN:0.5Ce,xTb with several different values of Tb^{3+} content. The inset shows the energy transfer efficiency versus Tb^{3+} content.

Tb^{3+} increases and has a maximum intensity at x = 0.5. The 5d–4f transition of Ce^{3+} is electric–dipole allowed and several orders of magnitude stronger than the forbidden 4f–4f electronic transitions within the 4fn configuration of Tb^{3+}. Therefore, Ce^{3+} can strongly absorb UV or near-UV radiation and efficiently transfer its energy to Tb^{3+} to enhance the emission of Tb^{3+}[4, 13,14,15]. The Ce^{3+} ions act as sensitizers and the Tb^{3+} ions as activators in this work. The same results can also be seen from Fig 4, which further supports the occurrence of the energy transfer from Ce^{3+} to Tb^{3+}. The energy levels of Tb^{3+} are suitable for energy transfer to take place from the allowed Ce^{3+} emission of 4f–5d upon excitation with 365-nm UV light. In the present system $BLN:Ce^{3+}$, Tb^{3+}, first Ce^{3+} ions are excited by UV light, then energy transfer takes place from Ce^{3+} to Tb^{3+}. Figure 6
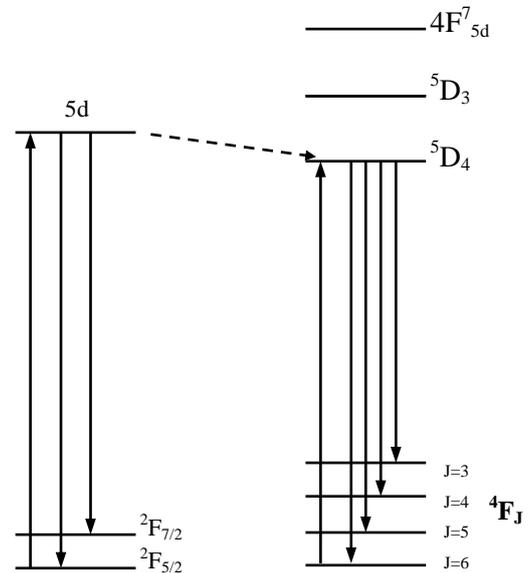

Fig 6. Energy-level scheme of BLN:Ce,Tb showing electronic transitions and energy transfer process

depicts the energy-level scheme with electronic transitions (Ce^{3+}, Tb^{3+}) and energy transfer process ($Ce^{3+} \rightarrow Tb^{3+}$). The optical properties of $BLN:Ce^{3+}$, Tb^{3+} are determined by the transitions between f-electron and d-electron states of cerium and between different f-electron states of terbium. Upon UV excitation, energy transfer takes place from 5d (Ce^{3+}) to the high excitation levels of Tb^{3+} (4fn) followed by the cross relaxation to the $^5D_4$ level of Tb^{3+}, which decays radiactively to various lower levels of ^7F_J (J=6,5,4,3) [2, 4].

IV. CONCLUSION

Spectroscopic properties of Tb^{3+} and Ce^{3+} ions doped alkali metal borate glasses $(70-x-y)B_2O_3.15Li_2CO_3.15Na_2CO_3.xTb_2O_3.yCeO_2$ (BLN:Ce,Tb) have been studied. The emission intensity of Ce^{3+} or Tb^{3+} in BLN:Ce or BLN:Tb glasses is influenced by the Ce^{3+} or Tb^{3+} doping content, and the optimum concentrations of Ce^{3+} and Tb^{3+} are 0.5 mol and 0.75 mol%, respectively. The concentration quenching effect of Ce^{3+} or Tb^{3+} in $BLN:Ce^{3+},Tb^{3+}$ glasses occurs. Concentration quenching mechanism is d–d

interaction for either Ce^{3+} or Tb^{3+}. The BLN:Ce^{3+},Tb^{3+} glasses can produce color emission from blue to green by properly tuning the relative ratio between Ce^{3+} and Tb^{3+}, and the emission intensity of Tb^{3+} in BLN:Ce^{3+},Tb^{3+} glasses can be enhanced by the energy transfer from Ce^{3+} to Tb^{3+}. The results indicate that the glasses BLN:Ce,Tb may have a potential application in white LED as double emitting glasses.

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