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Luminescence and energy transfer studies on Sm^{3+}/Tb^{3+} codoped telluroborate glasses for WLED applications

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ABSTRACT

A new series of Sm^{3+}/Tb^{3+} codoped telluroborate glasses have been prepared by conventional melt quenching technique with the chemical composition $(40-x-y)B_2O_3+15TeO_2+15Li_2O+15LiF+15NaF+xTb_2O_3+ySm_2O_3$ (where x = 0, 0.5; y = 0, 0.05, 0.1, 0.25, 0.5, 1 and 2 wt%). The structural and optical behaviour of the prepared glasses were investigated through Fourier transform infrared spectroscopy (FTIR), optical absorption, photoluminescence and lifetime measurements. The fundamental vibrational units of the borate and tellurite network have been identified through FTIR spectra. Nephelauxetic ratio ($\bar{\beta}$) and bonding parameter (δ) values indicate that the Sm–O bonds are ionic in nature. The characteristic emissions of terbium (543 nm, green) and samarium (645 nm, orange-red) were observed while exciting the Tb^{3+} ions. Higher magnitude of asymmetric intensity ratio (AIR) values confirms the higher asymmetry around the Sm^{3+} ion site. Decay profiles of Tb^{3+} ions ($^5D_4$ state) and Sm^{3+} ions ($^4G_{9/2}$ state) exhibit double exponential nature. The nature of interaction between the donor (Tb^{3+}) and acceptor (Sm^{3+}) has been analyzed through Inokuti-Hirayama (IH) model. Energy transfer from Tb^{3+} to Sm^{3+} ions is dominated by dipole-dipole type interaction. TBLT0.5S glass possess the better colour coordinates (0.41, 0.45) and colour correlated temperature (CCT) value (3524 K) and the same is suggested for eye safe warm white light emitting applications.

1. Introduction

Development of white light emitting diodes (WLEDs) based on trivalent rare earth (RE^{3+}) ions doped glasses has attracted great attention of researchers as they are expected to provide better colour rendering index and reduce the cost of WLEDs. Conventional WLEDs are fabricated using indium gallium nitride (InGaN) based blue LED chips coated with $Y_3A_{15}O_{12}:Ce^{3+}$ yellow phosphor. But these conventional WLEDs suffer on account of their poor energy conversion efficiency, lower luminescence intensity, poor colour rendering index, lower lifetime and lower stability [1]. These drawbacks have been overcome by fabricating the LEDs using rare earth doped glasses coupled with UV chips. The RE doped WLEDs find applications in LCD displays, fiber amplifiers, sensors etc. This is chiefly due to their high luminous efficiency, high brightness, lower attenuation coefficient, smaller size and longer lifetime [2].

We have chosen samarium and terbium ions in the present work for developing the white light applications as they lead to efficient light emission via charge transfer luminescence. The Tb^{3+} ion is one of the efficient optical activator that plays an important role in the field of photonics for the development of multicolour LEDs, plasma display panels, LED displays, laser, etc. It provides excellent green emission at 543 nm ($^5D_4 \rightarrow {}^7F_5$) with high quantum yield [3,4]. Trivalent samarium ions emit a strong reddish-orange emission ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) at 645 nm which is useful in high density optical memory storage devices, visible solid state lasers, medical radiation dosimetry, colour display systems, etc. [5]. Tb^{3+} ions are more suited for codoping with Sm^{3+} ions as the Tb^{3+} emission band has a large overlap with the Sm^{3+} excitation band. The Sm^{3+} ions are known for their characteristic reddish-orange emission which helps to improve the white light emission in terms of increasing the intensity of the red component. The energy transfer process that takes place between the donor (Tb^{3+}) and acceptor (Sm^{3+}) ions have lot of significance in the field of photonics. This process is explained in terms of emissions, decay lifetime, energy level diagram and energy transfer parameters. Further the energy transfer helps one to design photonic devices with

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Table 1
Physical properties of the Sm^{3+}/Tb^{3+} codoped telluroborate glasses.

Sl.No	Physical properties	TBLT0.05S	TBLT0.1S	TBLT0.25S	TBLT0.5S	TBLT1S	TBLT2S
1	Density (ρ) (g/cm^3)	2.847	3.095	2.968	3.033	3.085	3.184
2	Refractive index (η_d)	1.609	1.598	1.596	1.601	1.604	1.605
3	Rare earth ion concentration ($N \times 10^{20}$) (ions/cc)	0.238	0.516	1.229	2.555	4.962	9.864
4	Polaron radius (r_p) (Å)	14.008	10.823	8.104	6.350	5.090	4.048
5	Inter ionic distance (r_i) (Å)	34.765	26.861	20.113	15.759	12.631	10.046
6	Field strength ($F \times 10^{13}$) (cm^2)	2.482	4.158	7.416	12.079	18.803	29.727
7	Electronic polarizability ($\alpha_e \times 10^{-22}$)	34.749	15.793	6.613	3.202	1.656	0.834
8	Molar refractivity (R_m)	1.824	1.653	1.720	1.694	1.672	1.623
9	Dielectric constant (ε)	2.589	2.554	2.547	2.563	2.573	2.576
10	Reflection losses (R) (%)	5.449	5.298	5.271	5.339	5.380	5.394

desirable qualities. Generation of white light from the prepared glasses can be achieved by an appropriate combination of the dopants with suitable pump wavelengths.

The selection of suitable host matrix for the doping of RE ions is essential for photonic applications. Among the various host matrices, the borate based glasses are endowed with high transparency, excellent thermal stability, low melting point and higher phonon energy (1300–1500 cm^{-1}) than phosphate, tellurite and chalcogenide glasses [6]. This higher phonon energy is reduced by addition of tellurite content. The low phonon energy (600–800 cm^{-1}) of the telluroborate glasses reduces the non-radiative decay rate, which in turn enhances the fluorescence quantum efficiency of the RE ions. These glasses are endowed with good rare earth ion solubility and good optical properties [7].

Caldino et al. [8] prepared the Sm^{3+}/Tb^{3+} codoped sodium-zinc-aluminosilicate glasses via Ag^+–Na^+ ion-exchange. These glasses are useful for optical waveguides. Sm^{3+}/Tb^{3+} codoped oxyfluoridealuminoborate glasses were prepared and studied by Babu et al. [9]. They found that, the light emitted by these glasses could be tuned from cold to warm white light by increasing the concentration of Al_2O_3 or γ-irradiation. Liang et al. [10] examined the Sm^{3+}/Tb^{3+} codoped silicate and borosilicate glasses and reported white light emission under UV excitation. In their study of Sm^{3+}/Tb^{3+} codoped lead fluorotellurite glass by Bahadur et al. [11], could associate the energy transfer between the Tb^{3+} and Sm^{3+} ions to dipole-dipole interaction.

In the present work reports the luminescence and energy transfer studies on Sm^{3+}/Tb^{3+} codoped telluroborate glasses. The characteristic emission colour and CCT values of the prepared glasses were estimated as a function of Sm^{3+} ion concentration and changing the pump wavelengths. Energy transfer process takes place between the donor (Tb^{3+}) to acceptor (Sm^{3+}) ions were explored through IH model. Finally the prepared glasses were proposed to explore the feasibility of the white light emission.

2. Experimental methods

The Sm^{3+}/Tb^{3+} codoped telluroborate glasses have been prepared with the melt quenching technique following the procedure reported elsewhere [6]. The starting materials, H_3BO_3, TeO_2, Li_2CO_3, LiF, NaF, Tb_2O_3 and Sm_2O_3 (purchased from Sigma Aldrich, ~99.99% purity) were used without any further processing. The glass compositions and the codes are given below.

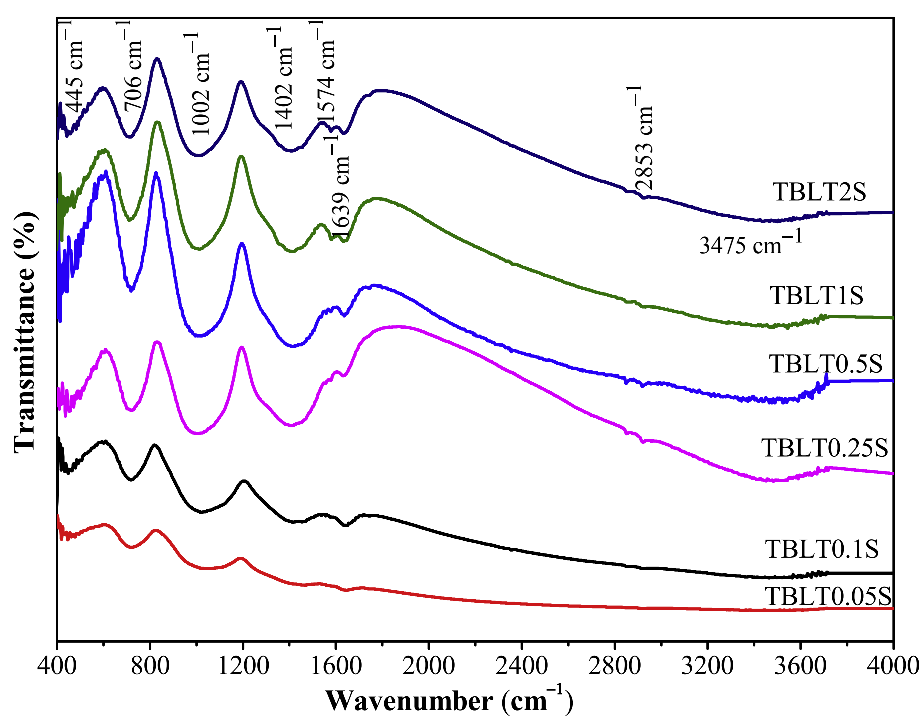

Fig. 1. FTIR spectra of the Sm^{3+}/Tb^{3+} codoped telluroborate glasses.