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Luminescence properties of Tb^{3+}–Sm^{3+} codoped glasses for white light emitting diodes

Xiaoluan Liang, Yunxia Yang, Chaofeng Zhu, Shuanglong Yuan, and Guorong Chen[a)]
Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

Allan Pring
Department of Mineralogy, South Australian Museum, North Terrace, Adelaide, South Australia 5000, Australia

Fang Xia
School of Chemical Engineering, University of Adelaide, Adelaide, South Australia 5005, Australia

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Photoluminescence properties of silicate and borosilicate glasses codoped with Tb^{3+} and Sm^{3+} ions have been characterized by excitation and emission spectroscopies. When excited by ultraviolet light the glasses emit a combination of green and orange-red wavelengths giving white light. The ratio of the intensities of orange-red to green emissions can be tuned by varying both the concentration of the Sm^{3+} ion and an the composition of the glass matrix. The excitation and emission spectra show a self-quenching effect for the Sm^{3+} ions and an energy transfer from Tb^{3+} ($^5D_4$) to Sm^{3+} ($^4G_{5/2}$). *© 2007 American Institute of Physics*. [DOI: 10.1063/1.2776857]

Glasses doped with rare earth ions (RE^{n+}) are proving to be luminescence materials as they have high emission efficiencies. These emissions correspond to $4f$-$4f$ and $4f$-$5d$ electronic transitions in the RE^{n+}.[1] The $4f$-$4f$ transition gives an especially sharp fluorescence pattern from the ultraviolet (UV) to the infrared region.[2,3] This is due to shielding effects of the outer $5s$ and $5p$ orbitals on the $4f$ electrons. In recent years, there has been an increasing trend for white light emitting diode (W-LED) to replace the conventional incandescent and fluorescent lamps due to advantages in energy use and related environmental benefits. At present, W-LEDs are fabricated by combining two or three different types of phosphors that can be excited by the blue LED chip.[4] The main problems with this type of W-LEDs are that the white light emissions tend to be unstable with respect to input power, the lower color rendering index can be poor, reproducibility are relatively low, and the luminescent efficiency reduces with time.[5] In order to overcome these problems, it is essential to devise luminescent materials that can directly emit white light under the excitation from the ultraviolet LED chip. Although phosphors have been widely investigated for this purpose, glasses could be considered as good alternatives for W-LED as they are simple to use and can be produced at a relatively low cost.[6]

In this work, a series of Tb^{3+}–Sm^{3+} codoped silicate and borosilicate glasses are described and their absorption of UV light and emission of white light are reported. In particular, the dependence of luminescence properties on the concentration of RE^{n+} activators and glass matrix compositions is discussed.

Seven glass samples are investigated in the present study. The samples were prepared using a conventional melt-quenching technique. High-purity powders of SiO_2, $CaCO_3$, $BaCO_3$ and/or H_3BO_3 (all analytical reagent), Tb_4O_7, and Sm_2O_3 (99.99%) were mixed according to the compositions shown in Table I to provide 50 g batches. Each batch was melted in an alumina crucible at 1550 °C for 2 h in air. The melt was then poured into a preheated stainless steel mold to form a 2 mm thick glass plate. To ensure their thermal and structural stabilities, all glasses were annealed at 500 °C for 2 h.

Both faces of each sample were polished before measurement of the excitation and emission spectra on a Fluorolog-3-P fluorescent spectrometer. All measurements were performed at room temperature using the same instrument parameters.

Emission spectra for samples Si1–Si7, excited with light of 375 nm, are shown in Figs. 1 and 2. The emission lines due to the Tb^{3+} and Sm^{3+} are evident. The Tb^{3+} emission bands include the peaks at 414, 437 (purple), 486 (blue), and 543 nm (green) and these are assigned to the electronic transitions of $^5D_3 \rightarrow {}^7F_5$, $^5D_3 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_6$, and $^5D_4 \rightarrow {}^7F_5$, respectively.[7] The Sm^{3+} emissions are at 563 (green), 601 (orange-red), and 648 (red) nm, and correspond to the $^4G_{5/2} \rightarrow {}^6H_{J/2}$ ($J=5,7,9$), electronic transitions.[8]

It can be seen from Fig. 1 that the emission intensity at 601 nm band correlates with the increasing Sm^{3+} concentration up to 1.5 mol % and then begins to fall away. This phenomenon implies the occurrence of the self-quenching effect (SQE) at concentration above 1.5 mol % in the silicate

TABLE I. Composition of analyzed glasses (mol %).

Glass No.	SiO_2	CaO	BaO	B_2O_3	Tb_4O_7	Sm_2O_3
Si1	50	37	13		0.125	0.25
Si2	50	37	13		0.125	0.50
Si3	50	37	13		0.125	0.75
Si4	50	37	13		0.125	1.00
Si5	40	37	13	10	0.125	0.75
Si6	40	37	13	10	0.125	0.50
Si7	40	37	13	10	0.125	0.25

[a)] Electronic mail: grchen@ecust.edu.cn

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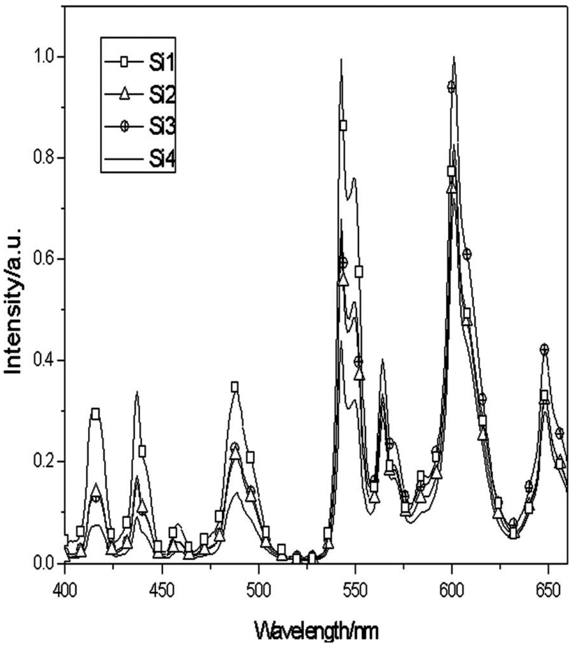

FIG. 1. Emission spectra for samples Si1–Si4 excited by 375 nm.

glasses due to interactions between the Sm^{3+} ions. Such a SQE is related to the ion-ion relaxation in Sm^{3+} ions and the possible mechanism for the energy transfer is dipole-dipole interactions.[9] A comparison with the borosilicate glasses (samples Si5–Si7) demonstrates that the SQE is also dependent on the glass composition. The strongest emission at 601 nm is for Sm^{3+} concentration of 0.5 mol % in the borosilicate glass (Fig. 2). It is well established that $[SiO_4]$ tetrahedra are the dominant structure units in the network of silicate glasses, and when B_2O_3 is added, B is mainly incorporated as planar $[BO_3]^-$ groups. If, however, alkali or alkaline earth oxides are added they provide nonbridging O^{2-} ions, then some of the B^{3+} ions can also exist as $[BO_4]^{3-}$ tetrahedra in the network.[10] The large ionic radii and high-field strength of RE^{n+} mean that they cannot occupy tetrahedral sites of the glass network, and they occupy sites of higher coordination number, for example, Sm^{3+} ion tends to occupy 8–11 coordinate sites in rare earth silicates minerals.[11] The three-dimensional (3D) frameworks of silicate glasses enable the Sm^{3+} ions to be well separated. In borosilicate glasses, however, the two-dimensional $[BO_3]$ triangles mean that the 3D framework is not so well developed and it is more likely that the Sm^{3+} ions cluster at lower concentration increasing the self-quenching probability.

TABLE II. Ratio of the intensities of the orange-red to the green emissions of samples.

Glass No.	Si1	Si2	Si3	Si4	Si5	Si6	Si7
Ratio	0.8307	1.2439	1.4705	1.6575	1.8196	1.5667	1.1388

There is a notable decrease in the intensity of Tb^{3+} emissions with increasing Sm^{3+} concentration in both the silicate and borosilicate glasses. In particular, there is a regular increase in the intensity ratio of the Sm^{3+} 601 nm emission to the Tb^{3+} 543 nm line even in the glasses with SQE (Table II). This is indicative of energy transfer from Tb^{3+} to Sm^{3+} occurring. This is supported by the fact that the energy level of Tb^{3+} ($^5D_4$) is a little higher than that of Sm^{3+} ($^4G_{5/2}$) (Fig. 3),[12] which makes energy transfer through the nonradiative processes possible.

This interpretation is consistent with the excitation spectra as they exhibit the similar characteristics for all samples. For example, the excitation spectra of sample Si3 monitored at 543 and 601 nm are given in Fig. 4 and the emission peak of Tb^{3+} at 487 nm has been included for comparison. The excitation peak at 377 nm, monitored at 543 nm, is due to the transition from the ground level $^7F_6$ to $^5D_2$ of Tb^{3+} ion while that at 374 nm, monitored at 601 nm, corresponds to the $^6H_{5/2} \rightarrow {}^4K_{13/2}$ electronic transition of the Sm^{3+} ion. Based on these two excitation spectra, it is believed that the UV radiation of wavelength around 375 nm could be used to efficiently excite these codoped glasses and this nicely

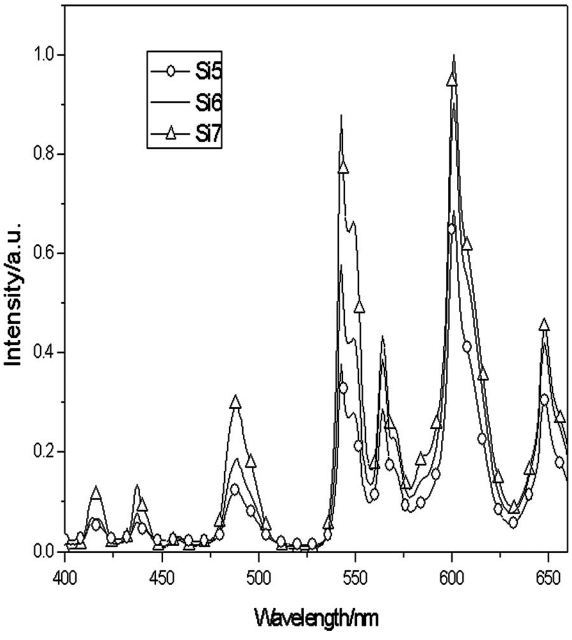

FIG. 2. Emission spectra for samples Si5–Si7 excited by 375 nm.

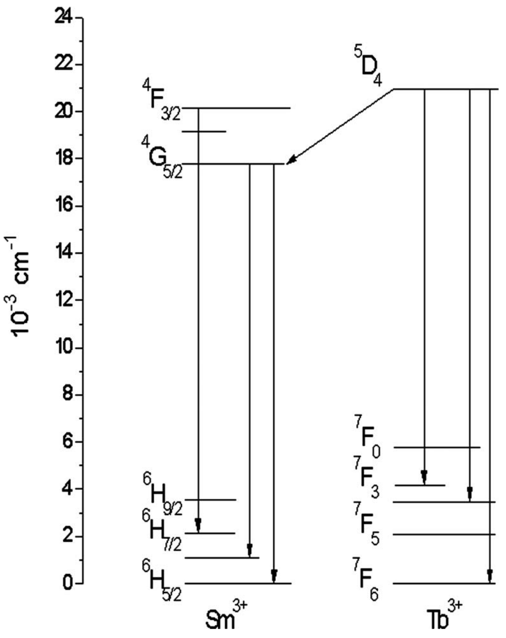

FIG. 3. Energy diagram of Tb^{3+} and Sm^{3+}.

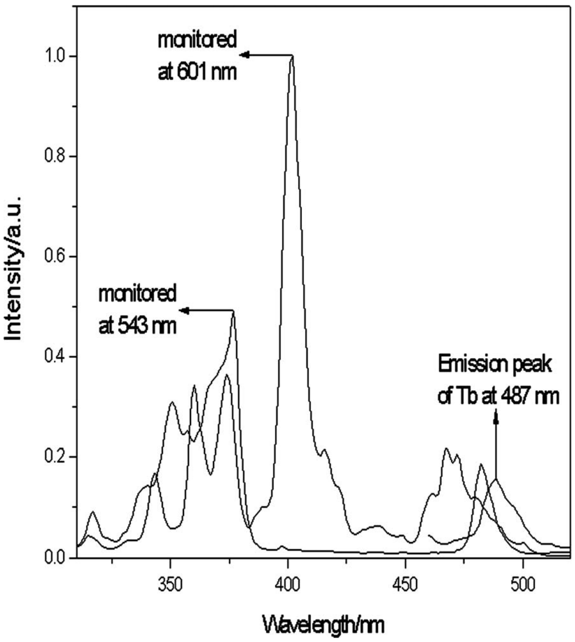

FIG. 4. Excitation spectra for sample Si3 monitored at 543 and 601 nm.

matches the requirements for W-LEDs. On the other hand, there is a broad excitation band for Sm^{3+} ions between 400 and 500 nm, overlapping with the blue emissions of Tb^{3+} ions. Thus the energy migration from Tb^{3+} (donor) to Sm^{3+} (acceptor) most likely occurs, resulting in the enhanced Sm^{3+} emissions at the cost of Tb^{3+} emission intensity. This process also accounts for the fact that both Tb^{3+} and Sm^{3+} emissions are stronger in the borosilicate glass sample (Si7) than in the silicate one (Si1) even though they contain the same concentrations of Tb^{3+} and Sm^{3+}. The presence of $[BO_4]^{3-}$ tetrahedra in the network of the glass (Si7) facilitates the ready reduction of Tb^{4+} to Tb^{3+} by heating in air at high temperature.[13] For the silicate glass (Si1), however, the lack of $[BO_4]^{3-}$ groups results in lower concentrations of Tb^{3+} and thus less total energy transfers to Sm^{3+}.

As noted above, the relative intensity of emissions (RIEs) from Tb^{3+} and Sm^{3+} vary with changing Sm^{3+} concentration (Table II). Another approach for RIE tuning is to adjust the glass matrix composition without changing the peak shape and position of the emissions. It can be seen that for the borosilicate glass (Si5), the emission intensity ratio of the orange-red (601 nm) to the green (543 nm) is 1.8196, higher than that of the silicate glass (Si3) (1.4705). That is, by replacing some of the SiO_2 by B_2O_3 in the glass composition, the orange-red emission can be enhanced relative to the green emission. It is therefore clear that chromaticity parameters of the present glasses can be tuned by changing both the activator concentration and the glass matrix composition. This is very important for lighting applications because the desired emission characteristics need to match with those of the International Commission on Illumination (CIE) chromaticity diagram.[14]

In summary, silicate and borosilicate glasses codoped with Tb^{3+} and Sm^{3+} ions were synthesized by the melt-quenching method. All luminescence glasses can be effectively excited by UV light. The self-quenching effects of Sm^{3+} ions are observed in the glasses and the critical concentration is dependent on glass composition. The energy transfer from Tb^{3+} ($^5D_4$) to Sm^{3+} ($^4G_{5/2}$) occurs through a nonradiative process. The intensity ratio of orange-red to green emissions can be tuned by varying both the concentration of Sm^{3+} ions and the composition of the glass matrix. Thereby, it is possible to generate the white light emission from these glasses by UV light excitation.

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