



Cerium and terbium ions doped strontium aluminosilicate polycrystalline phosphors



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ABSTRACT

Cerium and terbium ions doped strontium aluminosilicate polycrystalline phosphors with monoclinic structure identified to I2/c space group were synthesized by the high temperature solid-state reaction. Differential NUV-blue fluorescence behaviors of Ce³⁺ were exhibited under UVB radiation, which were originated from the luminescence centers with different crystal field environment. Bright green fluorescence of Tb³⁺ was released under UVA radiation, and with the intervention of Ce³⁺ ions, the effective excitation spectral range of Tb³⁺ ions was extended from UVA to UVB due to the energy transfer from Ce³⁺ to Tb³⁺. Upon the excitation in extended region, the luminescence intensity of Tb³⁺ was remarkably strengthened by a maximum fluorescence sensitization factor of ~152. These results demonstrate that Ce³⁺ and Tb³⁺ doped SrAl₂Si₂O₈ polycrystals are valuable NUV-blue and green phosphors, which have potential applications for phototherapy and color display.

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1. Introduction

Up to now, research activities in the field of trivalent rare earth (RE³⁺) ions doped phosphors have been carried out by many researchers to explore the capable of fulfilling several applications, namely security inspection equipment, optical sensing device, fluorescent lamp, biological labeling, white-LED and so on [1–7]. The 4f electronic configuration of RE³⁺ ions in numerous hosts provides emissions covering the ultraviolet and visible radiation regions [8–17]. The ultraviolet radiation is carried over into medical phototherapy source to treat various skin diseases such as psoriasis, vitiligo, scleroderma and cutaneous T-cell lymphoma, meanwhile, the visible emissions based on RE³⁺ ions activated phosphors can be utilized for solid-state display technique [18–26].

Selection of phosphor hosts is a key role for the optically active ions to develop admirable optical devices. Among the various phosphor hosts, aluminosilicate is more suitable for practical applications as a long-persistence host material with stable crystal structure, excellent chemical stability and strong oxidation resistance, which holds enormous research value [27–29]. In RE³⁺ ion family, Tb³⁺ ions, well-known activator, can present abundant emissions in visible spectral region owing to its rich energy level structure, while the Tb³⁺ ions exhibit weak fluorescence in the

UVB region because 4f-4f transition lacks the effective absorption in this spectral range [30–33]. Fortunately, Ce³⁺ ions have the strong 4f-5d absorption transition, which can be high efficiently excited and emit consuming NUV-blue fluorescence under UVB radiation, meanwhile, there is an overlap of energy band between Ce³⁺ and Tb³⁺, indicating that Ce³⁺ is expected to be a sensitizer that transfers a part of excitation energy to Tb³⁺. In other words, co-doping of Ce³⁺ in the hosts not only expands the effective excitation spectral range of Tb³⁺, but also increases the emission intensity of Tb³⁺ [34–44].

In this work, cerium and terbium ions doped strontium aluminosilicate polycrystalline phosphors have been synthesized, and the crystal structure with monoclinic system has been identified. Strong NUV-blue and green fluorescences were generated from the emitting of Ce³⁺ and Tb³⁺ in the phosphors, respectively. Difference of fluorescence emission behaviors was observed in the SrAl₂Si₂O₈:Ce³⁺ owing to the luminescence centers with distinct crystal field environment under UVB excitation. Because of strong absorption of Ce³⁺ ions in UVB waveband and efficacious energy supply to Tb³⁺ ions, co-doping of Ce³⁺ leads to the extension of effective excitation range for Tb³⁺ from UVA to UVB and an enhancement of Tb³⁺ emission intensity by the maximum sensitization factor of ~152 under UVB radiation. All results imply that Ce³⁺ and Tb³⁺ doped SrAl₂Si₂O₈ polycrystals are valuable NUV-blue and green phosphors, which have great promise for phototherapy and color display.

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2. Experiments

Ce^{3+} and Tb^{3+} doped $\text{SrAl}_2\text{Si}_2\text{O}_8$ phosphors were obtained by high temperature solid-state reaction. Reagents SrCO_3 (99.95%), Al_2O_3 (4N), SiO_2 (4N), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4N) and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4N) were employed as raw material, and 3 wt% H_3BO_3 (A.R) of raw material was added as flux. Stoichiometric amounts of the original chemical for $\text{Sr}_{1-x-y}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}, \text{yTb}^{3+}$ ($x=0.01\%, 0.05\%, 0.1\%, 0.3\%$; $y=0.1\%, 0.2\%, 0.5\%, 1.0\%, 2.0\%, 3.0\%$) were well-mixed together in an agate mortar. The starting material in alumina crucibles was heated in the reducing atmosphere, which contains carbon monoxide generated by carbon powder at 1250°C for 3 h. The synthesized samples were obtained after cooling down to room temperature, grinding into powder, and washing with water and alcohol.

The phase purity and the crystal structure of the powder were identified by X-ray diffraction (XRD) profiles, which were recorded by a Shimadzu XRD-7000 (Cu-K α , 40 kV, 30 mA) diffractometer. The 2θ ranges of all the data were set from 10° – 70° with a step size of 0.02° . A Hitachi F-7000 spectrometer was used to measure fluorescence (PL) and fluorescence excitation (PLE) spectra. The luminescence pictures of the samples were taken with a Sony Z2 mobile phone. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystalline phase analysis

The powder samples are checked by X-ray diffraction (XRD), and the typical XRD patterns of the $\text{SrAl}_2\text{Si}_2\text{O}_8$ host, $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.1\%$) and $\text{Sr}_{1-y}\text{Al}_2\text{Si}_2\text{O}_8:\text{yTb}^{3+}$ ($y=1.0\%$) are presented in Fig. 1, respectively. The synthesized phosphors are found to be consistent with the JCPDS standard card no.70-1862, and the crystal structure of synthesized phosphors is identified as $\text{SrAl}_2\text{Si}_2\text{O}_8$ polycrystal with the monoclinic space group I2/c. The cell parameters of $\text{SrAl}_2\text{Si}_2\text{O}_8$ host, $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.1\%$) and $\text{Sr}_{1-y}\text{Al}_2\text{Si}_2\text{O}_8:\text{yTb}^{3+}$ ($y=1.0\%$) are derived to be ($a=0.8370$ nm, $b=1.2993$ nm, $c=1.4261$ nm, $\beta=115.3333^\circ$), ($a=0.8382$ nm, $b=1.2993$ nm, $c=1.4272$ nm, $\beta=115.2699^\circ$), and ($a=0.8362$ nm, $b=1.3007$ nm, $c=1.4278$ nm, $\beta=115.4439^\circ$), respectively, and tiny difference among the cell parameters indicates that the RE^{3+} doping has little effect on cell structure of the host. In addition, the volume parameters of cell for the $\text{SrAl}_2\text{Si}_2\text{O}_8$ host, $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.1\%$) and $\text{Sr}_{1-y}\text{Al}_2\text{Si}_2\text{O}_8:\text{yTb}^{3+}$ ($y=1.0\%$)

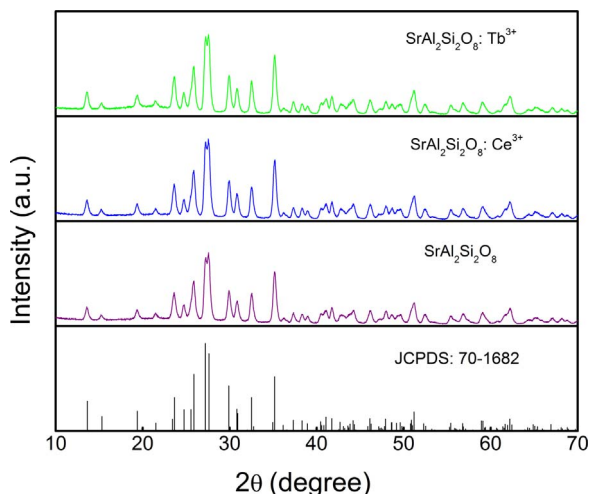


Fig. 1. XRD patterns of the $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.1\%$) and $\text{Sr}_{1-y}\text{Al}_2\text{Si}_2\text{O}_8:\text{yTb}^{3+}$ ($y=1.0\%$) polycrystalline powders.

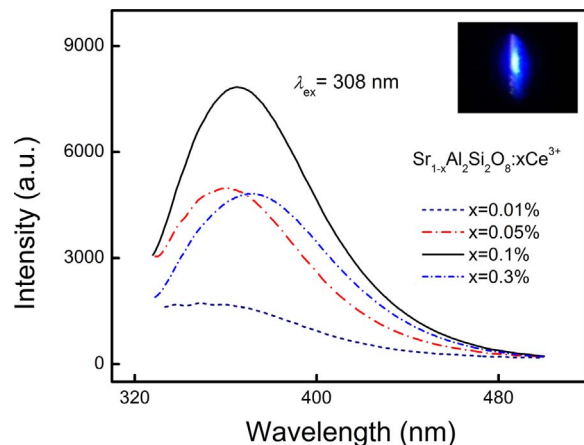


Fig. 2. PL spectra of $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.01\%, 0.05\%, 0.1\%, 0.3\%$) phosphors. Inset: photograph of $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.1\%$) under 308 nm excitation.

are 1.4018, 1.4056 and 1.4023 nm^3 , respectively, which can be seen that the slight swelling of space structure is caused and the expansion rate of the polycrystal is less than 0.3% with the introduction of RE^{3+} ions.

3.2. Photoluminescence properties of Ce^{3+} doped $\text{SrAl}_2\text{Si}_2\text{O}_8$

Efficient NUV-blue fluorescence is achieved in the $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.1\%$) polycrystalline phosphors, as shown in the inserted photo of Fig. 2. The PL spectra of $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.01\%, 0.05\%, 0.1\%, 0.3\%$) are depicted in Fig. 2. The results illustrate that all of them are broad band spectra, and the emission centered at 366 nm is attributed to the $5d \rightarrow 4f$ transition of Ce^{3+} [45]. A redshift about 23 nm with increasing of Ce^{3+} concentration from 0.01% to 0.3% is exhibited by comparing the emission spectra of Ce^{3+} doped $\text{SrAl}_2\text{Si}_2\text{O}_8$. Although the shift of peak wavelengths is associated with the self-absorption of phosphors, the dominant reason is that Ce^{3+} ions form luminescence centers with different properties in the $\text{SrAl}_2\text{Si}_2\text{O}_8$ host due to crystalline environment change following the increase of Ce^{3+} concentration [46].

The two typical luminescence emissions of $\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8:\text{xCe}^{3+}$ ($x=0.1\%$) monitored at 280 nm and 325 nm are presented in Fig. 3(a), respectively. Under excitation of 280 nm radiation, the high-energy emission peak seated at 348–378 nm was split into two groups of subbands by Gaussian fitting in the wavenumber space as shown in Fig. 3(b). Among them, one group situated at 31025 and 29000 cm^{-1} and the other located at 26810 and 25103 cm^{-1} , and the energy differences between the peak values of two subbands in each group are 2025 and 1707 cm^{-1} , respectively, coinciding with the energy differences of transitions $5d \rightarrow {}^2F_{5/2}$ and $5d \rightarrow {}^2F_{7/2}$. It means that $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Ce}^{3+}$ has two luminescence centers with different natures, and the group of peaks located at 31025 and 29000 cm^{-1} is attributed to Ce(I) and another peaked at 26810 and 25103 cm^{-1} is ascribed to Ce(II). In view of the above, the emission band centered at 348 nm under 280 nm excitation is derived from the cooperation of both Ce(I) and Ce(II), and the emission band located at 378 nm under 325 nm excitation is mainly contributed to Ce(II).

Fluorescence emission behavior is closely related to the coordination field, and the coordination environment around Ce^{3+} ions can be evaluated by [47]

$$E = Q \left[1 - (V/4)^{1/V} 10^{-n \cdot ea \cdot r/8} \right], \quad (1)$$

where Q is the position in energy for the lowest d-band edge for free ion and the value is 50000 cm^{-1} for Ce^{3+} , V is the valence of activator

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