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Luminescence properties and energy transfer in AlN:Ce³⁺, Tb³⁺ phosphors

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ABSTRACT

Novel green-emitting AlN:Ce³⁺, Tb³⁺ phosphors were successfully synthesized by a solid-state reaction method. Single doped AlN:Ce³⁺ and AlN:Tb³⁺ phosphors could be effectively excited by ultraviolet lights and showed intense blue and green emissions, respectively. The incorporation of Ce³⁺ could drastically enhance the luminescence of AlN:Tb³⁺ powder by energy transfer. The effects of Ce³⁺ and Tb³⁺ concentrations on luminance in single and co-doped phosphors have also been studied. Analysis of the emission and excitation spectra, in conjunction with the curves of decay times, suggested that the effective energy transfer from Ce³⁺ to Tb³⁺ is mainly due to a dipole–dipole interaction in the AlN:Ce³⁺, Tb³⁺ phosphors.

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1. Introduction

Light-emitting diodes (LEDs) have gained increasing importance in daily life because of their superior lifetime, efficiency, reliability, and low pollution footprint [1–3]. Aluminum nitride (AlN) has been widely used as an electronic packing and a high thermal conductivity ceramic substrate owing to its high electrical insulation, high thermal conductivity, low thermal expansion coefficient, and physical and chemical stability [4,5]. Because of the wide band gap (6.2 eV), AlN is also considered as a potential candidate material for electroluminescence devices [6]. Recently, AlN thin films or phosphors doped with Er³⁺, Gd³⁺, Tb³⁺, Eu²⁺, and Ce³⁺ have been developed [7–9], which can be used in different types of LEDs.

White-LEDs, such as the blue-light In–Ga–N LED chip loaded with a yellow phosphor YAG:Ce [10], which are commercially available nowadays, exhibit a poor color rendering index (CRI) and high correlated color temperature owing to the lack of the red component [11,12]. An ultraviolet (UV) chip with red, green, and blue phosphors can overcome these weaknesses because this technology features higher CRI and high tolerance to the UV chip's

color variation with respect to the white color obtained only by the phosphors [13,14]. Accordingly, the development of novel multi-color emission phosphors is in great demand in the field of optical materials.

Energy transfer from a donor to an acceptor is a very important phenomenon in luminescence. The absorption and the emission of Ce³⁺ ions are very efficient in many hosts because of the allowed 4f to 5d broadband transitions. On the other hand, Ce³⁺ can greatly enhance the emission of Tb³⁺. This is important because CeO₂ is an inexpensive oxide; thus, it can effectively replace the expensive Tb₄O₇. Consequently, Ce³⁺ and Tb³⁺ seem to be an attractive pair for acting as the sensitizer and activator, respectively, for energy transfer from Ce³⁺ to Tb³⁺ in various hosts [15–22].

To our knowledge, there is no report documenting the photoluminescence of a Ce³⁺/Tb³⁺ co-doped AlN host. In this paper, we present the production of AlN phosphors, which were single-doped with Ce³⁺ and Tb³⁺, and co-doped with Ce³⁺/Tb³⁺, by the solid-state reaction method. The produced co-doped phosphors had a general formula of Ce_xTb_yAl_{1–x–y}N, where Ce concentration was 0.5% and Tb concentration ranged between 0.2% and 4.0%. The photoluminescence properties and the decay times of the produced phosphors were determined experimentally. The experimental results are thoroughly analyzed and discussed to shed light on the mechanism and the efficiency of energy transfer from Ce³⁺ to Tb³⁺ in the produced AlN:Ce³⁺, Tb³⁺ phosphors.

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2. Materials and experimental procedure

Fine powders of AlN, CeO₂, and Tb₄O₇ (all from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), in amounts according to the aforementioned formulae, were thoroughly mixed in a BN mortar. The homogenous powder mixtures were placed in BN crucibles; then, the crucibles were placed in a carbon tube furnace and fired under flowing N₂ gas for 4 h at 1700 °C. The heating and the cooling rates were 300 K/h.

The developed phases in the produced powders were identified in an X-ray diffractometer (XRD, Philips PW 1700) using Cu K_{α1} radiation at a scanning rate of 0.5 degrees/min. The photoluminescence spectra were recorded at room temperature by a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Japan) with a 200 W Xe lamp as the excitation source. The emission spectra were corrected for the spectral response of a monochromator and Hamamatsu R928P photomultiplier tube (Hamamatsu Photonics K.K., Hamamatsu, Japan) by a light diffuser and tungsten lamp (Noma Electric Corp., NY; 10V, 4A). The excitation spectra were corrected for the spectral distribution of the xenon lamp intensity by measuring Rhodamine-B as reference. The decay time spectra were recorded on a spectrophotometer (FLS920, Edinburgh Instruments Ltd.).

3. Results and discussion

The diffractograms of Fig. 1 suggest that AlN (JCPDS No. 00-025-1133, space group: P6₃mc) was formed exclusively in the produced powders in the cases of the phosphors with 0.5% Ce, 0.5% Tb and the co-doped phosphors. With respect to the diffractogram of pure AlN, doping caused a shift of the peaks toward smaller angles, which is clearly seen in the inset of Fig. 1. This suggests that Ce³⁺ and Tb³⁺ were accommodated in the lattice of AlN.

The excitation and emission spectra of single-doped AlN:xCe³⁺ (for x = 0.2%, 0.5%, and 1.0%) and AlN:yTb³⁺ (for y = 0.2%, 0.5%, and 1.0%) phosphors are plotted in Figs. 2 and 3, respectively. It can be seen that the emission intensity increases with the increase of the concentration of Ce³⁺ (Tb³⁺) up to x(y) = 0.5% and then it decreases (for x(y) = 1.0%). This is attributed to concentration quenching.

The excitation spectra of AlN:Ce³⁺ monitored at 437 nm (Fig. 2) have an intense band with two peaks, at ca. 280 and 305 nm, attributed to the 4f–5d transition of Ce³⁺ ions. Moreover, upon excitation at 280 nm, the emission spectra display an asymmetric

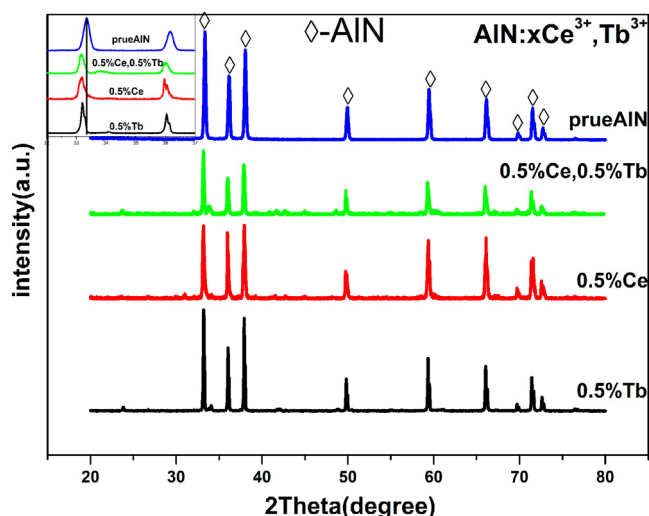


Fig. 1. X-ray diffractograms of AlN:xCe³⁺,yTb³⁺ phosphors produced at 1700 °C (4 h). The inset shows the shift of the peaks positions.

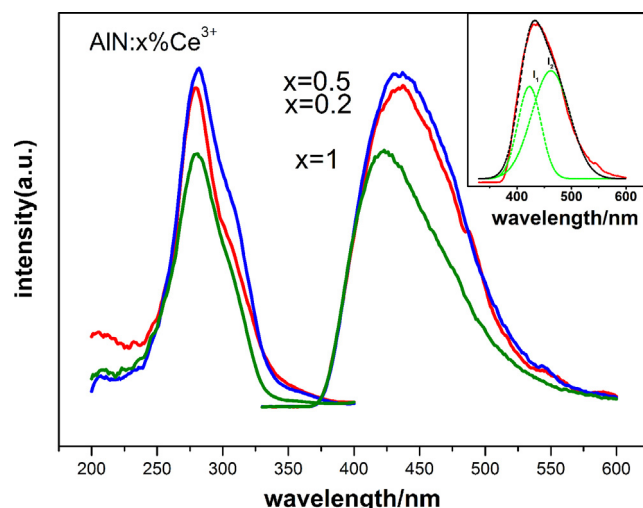


Fig. 2. Excitation and emission spectra of AlN:xCe³⁺ phosphors. The inset shows the emission spectrum of AlN:0.5%Ce³⁺ and its Gaussian components at 422 nm (*I*₁), 463 nm (*I*₂).

broad band with a maximum at ca. 437 nm, which should be due to the 5d–4f transitions in Ce³⁺. The asymmetric emission band can be decomposed into two Gaussian components peaking at 422 nm (*I*₁) and 463 nm (*I*₂), which are shown in the inset of Fig. 2. The energy difference of 2090 cm^{−1} indicates that these two peaks are due to the splitting of 4f ground state of Ce³⁺, since the energy gap between the ²F_{7/2} and ²F_{5/2} levels in Ce³⁺ ion is about 2000 cm^{−1} in most Ce³⁺ activated phosphors. According to an earlier study, the Ce³⁺ ion should be located at the center of the octahedral interstices [23].

The AlN:yTb³⁺ phosphors (Fig. 3) show two absorption peaks at 285 and 301 nm, attributed to the spin-allowed 4f⁸–4f⁷5d transitions of Tb³⁺ ions. There are also characteristic sharp emission lines centered at 485, 543, 580, and 619 nm, which should be results of the transitions from the ⁵D₄ level to the ⁷F₆, ⁷F₅, ⁷F₄, and ⁷F₃ levels of Tb³⁺, respectively [24].

Fig. 4 shows the influence of co-doping on the emission spectra of the produced AlN:xCe³⁺,yTb³⁺ phosphors. Firstly, the characteristic blue emission band due to Ce³⁺ and the green emission peaks due to Tb³⁺ are clearly observed in all the spectra recorded from the co-doped phosphors under excitation at 280 nm UV light. In the

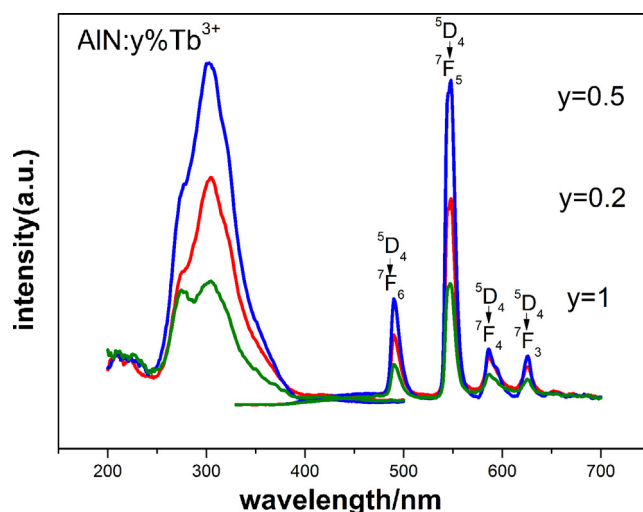


Fig. 3. Excitation and emission spectra of AlN:yTb³⁺ phosphors.

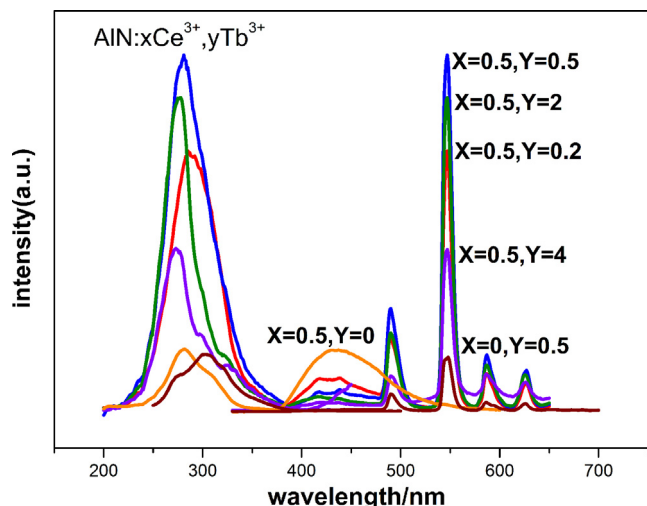


Fig. 4. Excitation and emission spectra of AlN: $x\text{Ce}^{3+}$, $y\text{Tb}^{3+}$ phosphors, single-doped and co-doped.

co-doped phosphors, the presence of Ce^{3+} ions causes a pronounced increase (almost 6 times higher) in the emission intensity compared with the intensity of the single- Tb^{3+} -doped phosphor. When Ce^{3+} concentration is fixed at 0.5% and the concentration of Tb^{3+} increases, then (a) the emission intensity due to Ce^{3+} decreases monotonically, and (b) the emission intensity due to Tb^{3+} is improved considerably, reaches a maximum for a Tb^{3+} concentration equal to 0.5% and then it decreases, likely due to concentration quenching. This finding suggests that the quenching concentration of Tb^{3+} is 0.5%, which agrees fairly well with that observed in the AlN: Tb^{3+} phosphors (Fig. 3).

The above result also provides evidence for the energy transfer probability from Ce^{3+} ions to Tb^{3+} ions. In particular, Ce^{3+} ions can harvest high-energy UV photons from the excitation source, which are subsequently down-converted to low-energy visible photons that enhance the emission of Tb^{3+} ions. The energy transfer efficiency (η_T) from Ce^{3+} to Tb^{3+} in AlN phosphors can be calculated with the formula [25]

$$\eta_T = 1 - \frac{I_S}{I_{S0}} \quad (1)$$

where I_S and I_{S0} are the luminescence intensities of the Ce^{3+} (sensitizer) with and without the presence of Tb^{3+} , respectively. Using the values of the intensities of the bands in the spectra of Fig. 4, the values of η_T from Ce^{3+} to Tb^{3+} in AlN: 0.005Ce^{3+} , $y\text{Tb}^{3+}$ were calculated as 0, 44.9%, 79.6%, 92.3%, and 97.4% (for $y = 0, 0.002, 0.005, 0.02$, and 0.04 , respectively). It can be seen clearly that the value of η_T increases gradually with the increase of Tb^{3+} concentration. Consequently, the results of the present study suggest the occurrence of a very efficient energy-transfer process from Ce^{3+} to Tb^{3+} in AlN.

The photoluminescence decay curves shed light on the energy transfer between Ce^{3+} and Tb^{3+} . The decay curves for the single-doped phosphor with Ce^{3+} and the co-doped phosphors with a varying molar concentration of Tb^{3+} ($x = 0.005$; $y = 0, 0.002, 0.005, 0.02$ and 0.04 ; shown in Fig. 5) excited at 280 nm and monitored at 437 nm were recorded. The decay curves of Ce^{3+} ions fit well to a double-exponential function as

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + I(0) \quad (2)$$

Using the formula for τ

$$\tau = \frac{(A_1 \tau_1^2 + A_2 \tau_2^2)}{(A_1 \tau_1 + A_2 \tau_2)} \quad (3)$$

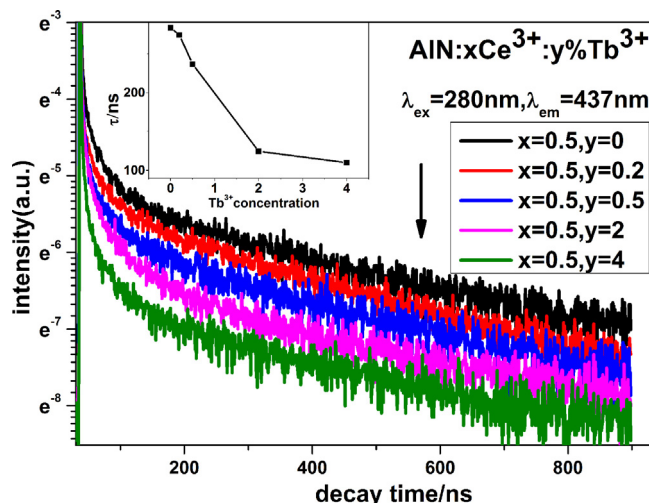


Fig. 5. Decay curves of the Ce^{3+} emission at 437 nm in AlN: Ce^{3+} , Tb^{3+} under excitation at 280 nm. The inset shows the dependence of the respective lifetime of Ce^{3+} on the Tb^{3+} concentration in AlN: Ce^{3+} , Tb^{3+} .

the calculated lifetimes were 283.5, 274.3, 236.8, 124.5 and 109.8 ns, respectively (inset of Fig. 5). It is generally accepted that energy transfer can be due to radiative transfer and due to non-radiative transfer. If resonant radiative transfer involves, then the lifetime of the donor should remain constant in the presence of the acceptor [26]. The decay curves due to Ce^{3+} in AlN: Ce^{3+} , Tb^{3+} phosphors, show that the lifetime owing to Ce^{3+} decreases monotonically with the increase of the concentration of Tb^{3+} ions. Accordingly, this suggests that the energy transfer from Ce^{3+} to Tb^{3+} should be predominantly due to non-radiative resonant energy transfer.

There are two main aspects with regard to the resonant energy-transfer mechanism. The first assumes the occurrence of exchange interactions and the second assumes electric multipolar interactions [27]. The requirements for exchange interactions are (i) a large, direct or indirect, overlapping of the orbitals of the sensitizer and the activator and (ii) the critical distance R_C to be shorter than 4 \AA [27]. Note that, in many cases, concentration quenching is due to energy transfer among the activators until an energy sink in the lattice is reached [28].

According to Blasse [29], the critical distance R_C can be calculated using the concentration quenching method, expressed by Eq. (4)

$$R_C = 2 \times \left(\frac{3V}{4\pi X_c N} \right)^{1/3} \quad (4)$$

where V is the volume of the unit cell, N is the number of the available sites for the dopant in the unit cell, and X_c is the total concentration of Ce^{3+} and Tb^{3+} ions. Thus, in the AlN: Ce^{3+} , Tb^{3+} phosphors of the present study, the critical distance of energy transfer is calculated as 15.86 \AA . As this value is markedly longer than 4 \AA , it is suggested that energy transfer should be rather unlikely to take place via the exchange interaction mechanism. Therefore, the energy transfer between the Ce^{3+} and Tb^{3+} ions should largely take place via electric multipolar interactions.

According to Dexter's energy transfer expressions for multipolar interactions, the following relation can be given [28]

$$\frac{\eta_{S0}}{\eta_S} \propto C^{n/3} \quad (5)$$

where η_{S0} and η_S are the luminescence quantum efficiencies of the Ce^{3+} ions without and with the presence of Tb^{3+} , respectively,

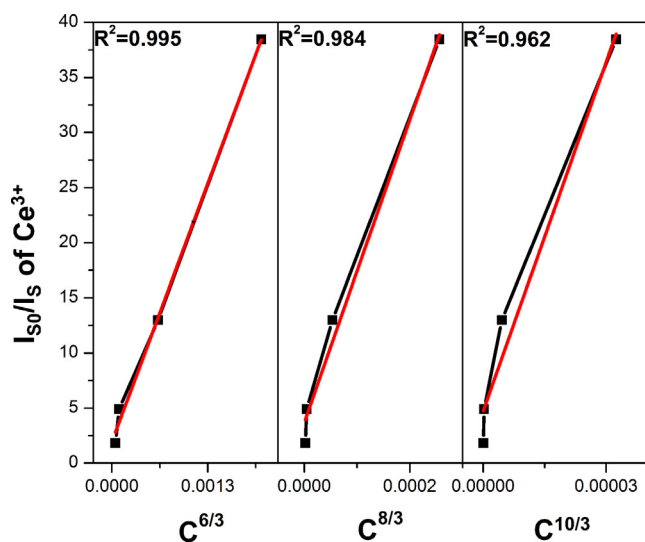


Fig. 6. Dependence of the linear fitting in the plot of I_{50}/I_S versus $C^{n/3}$ on the value of n , for $n = 6$, $n = 8$, and $n = 10$.

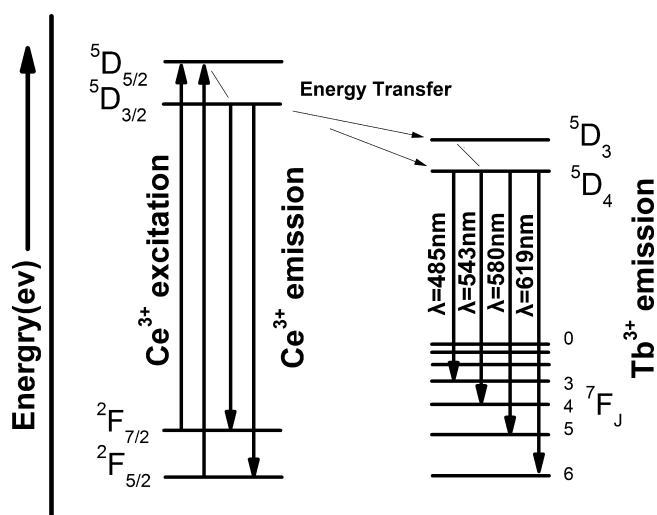


Fig. 7. Energy level diagram, which aims to show the luminescent mechanism in Ce^{3+} , Tb^{3+} co-doped AlN.

and C is the total dopant concentration of Ce^{3+} and Tb^{3+} ions. The values of n are 6, 8, and 10, for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively.

The values of the ratio of η_{50}/η_S can be approximately calculated by the ratio of related luminescence intensities (I_{50}/I_S). Fig. 6 illustrates the plots of I_{50}/I_S versus $C^{n/3}$ for $n = 6$, 8, and 10. It can be seen clearly that the best linear fitting is achieved for $n = 6$. This finding suggests that the energy transfer from the Ce^{3+} to the Tb^{3+} ions should be mainly due to a dipole–dipole interaction.

The luminescent mechanism in the $\text{AlN}:\text{Ce}^{3+}, \text{Tb}^{3+}$ phosphors can be interpreted with the aid of the energy level diagram presented in Fig. 7. The two excitation peaks in Fig. 2 originate from the two transitions $2F_{5/2}-5d$ and $2F_{7/2}-5d$. The energy transfers from the Ce^{3+} $5d$ to the Tb^{3+} $5d$ via a non-radiative way, resulting in the emission of green light, which corresponds to the transition from the $5D_4$ level to the $7F_6$, $7F_5$, $7F_4$, and $7F_3$ levels of Tb^{3+} . There was no evidence of emission in the blue region that might originate from the high-energy level $5D_3$. Because the $5D_3$ level to $5D_4$ level

transition is resonant with the $7F_6$ to $7F_0$ transition, the emissions of $5D_3$ to $7F_J$ transitions are often quenched in high Tb^{3+} concentration doped samples owing to the cross relaxation $5D_3 + 7F_6 \rightarrow 5D_4 + 7F_0$ [26].

4. Conclusions

In this paper, $\text{AlN}:\text{Ce}^{3+}, \text{Tb}^{3+}$ phosphors were successfully prepared by the solid-state reaction method. The emission spectra consist of a blue band that peaks at 437 nm and a green band with a peak at 547 nm, which originate from the transitions of Ce^{3+} ions and the Tb^{3+} ions, respectively. The analysis and the interpretation of the emission and the excitation spectra together with the decay curves suggest the occurrence of energy transfer from Ce^{3+} to Tb^{3+} , which is predominantly governed by a dipole–dipole interaction mechanism. The experimental results qualify the produced $\text{AlN}:\text{Ce}^{3+}, \text{Tb}^{3+}$ phosphors for further consideration and experimentation for potential use in the technology of white light-emitting diodes.

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