



Spectral and thermal properties of Dy³⁺-doped NaGdTiO₄ phosphors

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ABSTRACT

Dy³⁺-doped NaGdTiO₄ phosphors were synthesized by a solid-state reaction method. The crystal structure, spectral properties and fluorescence quenching of the phosphors were systematically studied by means of X-ray diffraction (XRD) and spectroscopy. It was found that the phosphors can be effectively excited by 281 nm ultraviolet light, and intense white light emission was observed. The white light was generated by mixing blue (483 nm) and yellow (578 nm) emissions corresponding to the transitions from ⁴F_{9/2} to ⁶H_{15/2} and ⁶H_{13/2} levels of Dy³⁺. The electric dipole–dipole interaction between Dy³⁺ ions was identified as the main mechanism for the concentration dependent fluorescence quenching of ⁴F_{9/2} level. The CIE color coordinates of the phosphors were calculated to be (x = 0.3345, y = 0.3535) in the white region under 281 nm excitation, which is very close to the E point (energy equal point, x = 0.3333, y = 0.3333). In addition, the thermal quenching behavior of ⁴F_{9/2} level of Dy³⁺ was also discussed, and the crossover effect was confirmed to be the dominant physical mechanism responsible for the fluorescence temperature quenching of Dy³⁺ in NaGdTiO₄ host.

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1. Introduction

In recent years, white light emitting diodes (WLEDs) have received lots of attention driven by their potential applications in the fields of panel display, field-emission display and solid-state lighting (SSL) owing to their superior properties, such as energy saving, reliability and safety [1–7]. White light can be generated in several manners, and the most common route for obtaining white light is to combine the blue light from GaN-based LED and the yellow light from YAG:Ce³⁺ phosphor excited by GaN LED. However, such WLEDs have a few problems discussed in previous reports [8–10]. To solve such problems, considerable efforts have been devoted to research on the rare earth (RE) ions doped luminescent materials, since RE ions possess abundant energy levels from which multicolor emissions covering ultraviolet (UV), visible and infrared wavelength region can be achieved.

Additionally, thermal stability is one of the most important characteristics for phosphors especially the one applied in phosphor converted WLEDs, since the WLEDs may operate at high

temperature, then the light output and color rendering index are easily deteriorated. Therefore, the development of a suitable phosphor for WLEDs and examine its fluorescence thermal stability is necessary.

Trivalent dysprosium ion (Dy³⁺) as a promising activator for white light emitting materials has been extensively studied due to its peculiar blue and yellow emission bands in the emission spectrum [11–17]. The blue band centered at around 484 nm corresponds to the ⁴F_{9/2} → ⁶H_{15/2} transition, and the yellow band located at around 575 nm corresponds to the hypersensitive transition ⁴F_{9/2} → ⁶H_{13/2}. The crystal field environment of Dy³⁺ has remarkable influences on the intensity of yellow emission, but has little effect on that of the blue emission. Therefore, it is possible to obtain white light emission from Dy³⁺-activated luminescent materials by changing the intensity ratio of yellow to blue emissions (Y/B) via changing the matrix or adjusting the host compositions [18].

In this paper, titanate was chosen as the host due to its special properties, such as low cost, easy preparation, excellent thermal and chemical stabilities, and especially the strong absorption in the near-UV region and effective energy transfer from host lattice to the activator [19]. Dy³⁺-doped NaGdTiO₄ phosphors were synthesized by a solid-state reaction method. Intense white light was obtained under 281 nm UV light excitation. The energy transfer, fluorescence quenching, chromatic properties and thermal quenching behavior of the phosphors were systematically discussed.

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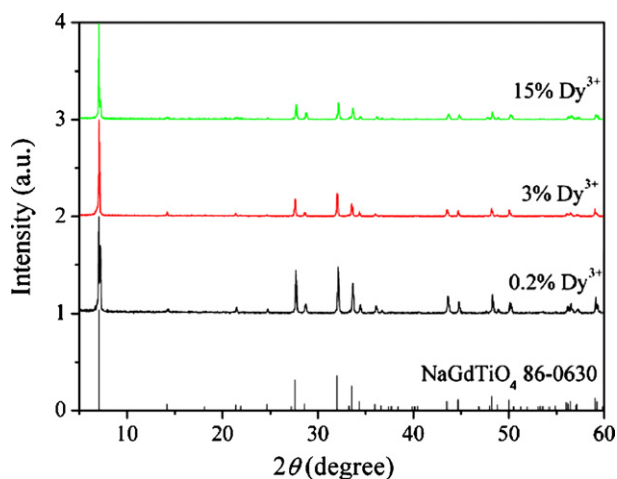


Fig. 1. Normalized XRD patterns of NaGdTiO₄ phosphors doped with 0.2, 3 and 15 mol% Dy³⁺ (top part) and the standard pattern of orthorhombic NaGdTiO₄ (bottom part).

2. Experimental

2.1. Sample preparation

Dy³⁺-doped NaGdTiO₄ phosphors were prepared by a solid-state reaction method in air atmosphere. The starting materials of Na₂CO₃, Gd₂O₃, TiO₂ and Dy₂O₃ powders were weighed according to certain stoichiometric ratios. The Dy³⁺ doping concentrations were 0.2, 0.6, 1, 3, 5, 7, 9, 12 and 15%, which are the molar percentage of Gd³⁺ replaced by Dy³⁺. The weighed starting materials were well mixed and then calcined at 1000 °C for 4 h. A detailed preparation procedure could be found elsewhere in Ref. [20].

2.2. Sample characterization

The crystal structure of the obtained phosphors were characterized by a SHIMADZU XRD-6000 (X-ray diffractometer) with Cu Kα (λ = 1.5406 Å) radiation. The XRD data in the 2θ ranging from 5° to 60° were collected with a scanning step of 0.02° and a scanning rate of 4.0° min⁻¹. The fluorescence spectra of the phosphors were obtained by Hitachi F-4600 fluorospectrophotometer with a 150 W Xe-lamp as an excitation source. This fluorospectrophotometer was well intensity-calibrated for the excitation and emission spectra. A modified temperature-controllable system assembled in our lab was used to heat the studied samples. With this system the sample temperature can be well adjusted and controlled in the region from 110 to 450 °C.

3. Results and discussion

3.1. Structural properties

In order to identify the crystal structure of the obtained samples, XRD measurements for all the samples with various Dy³⁺ concentrations were carried out, and very similar diffraction pattern for each sample was observed. Fig. 1 presents the normalized XRD patterns of the as-synthesized NaGdTiO₄ phosphors doped with 0.2, 3 and 15 mol% Dy³⁺ as a representative, together with the standard pattern of orthorhombic structure NaGdTiO₄ (JCPDS 86-0830). As can be seen, all of the observed diffraction peaks from each as-synthesized sample are in accordance with the ones of orthorhombic phase NaGdTiO₄ reported in JCPDS card. No extraneous phase emerged in the pattern, indicating that the starting materials completely reacted and the final NaGdTiO₄ products are well crystallized.

3.2. Fluorescence properties

Fig. 2 shows the excitation spectra (within the range of 200–500 nm) of NaGdTiO₄ phosphors doped with various Dy³⁺ concentrations. The monitored emission wavelength for all samples

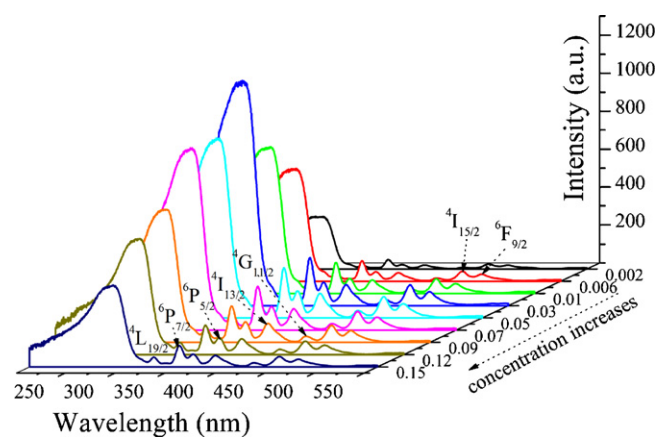


Fig. 2. Excitation spectra of NaGdTiO₄ phosphors doped with various Dy³⁺ concentration monitoring at 578 nm emission.

is one of the dominant emission wavelength 578 nm corresponding to the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition of Dy³⁺. It can be seen that all of the excitation spectra have the same profile in addition to the intensity. Each excitation spectrum is composed of a broad band located at 200–300 nm with a maximum intensity value at wavelength 281 nm, and a series of sharp peaks ranging from 300 to 500 nm. The broad band in the excitation spectra can be ascribed to the absorption of the excitation energy by the NaGdTiO₄ host lattice (TiO₄⁴⁻ complex ion) [21]. This phenomenon is similar with the cases of WO₄⁴⁻ and MO₄⁴⁻ groups, viz. NaGdTiO₄ host lattice first absorbs the excitation energy and then transfers the energy to the activator Dy³⁺. The sharp lines belong to the intrinsic *f–f* transitions of Dy³⁺ within its 4f⁶ configuration. The peaks located at 325, 351, 366, 388, 427, 451 and 471 nm correspond to the transitions from ⁶H_{15/2} ground state to ⁴L_{19/2}, ⁶P_{7/2}, ⁶P_{5/2}, ⁴I_{13/2}, ⁴G_{11/2}, ⁴I_{15/2} and ⁶F_{9/2} excited states, respectively. It should be noted that the intensity of the broad band coming from NaGdTiO₄ host lattice is much stronger than that of Dy³⁺ *f–f* transitions, suggesting that the excitation energy can be effectively transferred from host lattice to luminescent centers Dy³⁺. Therefore, we conclude that Dy³⁺-doped NaGdTiO₄ phosphor may be a potential phosphor for white light emitting devices based on UV LEDs.

Fig. 3 depicts the emission spectra of Dy³⁺-doped NaGdTiO₄ phosphors with various concentrations excited by 281 nm UV light. It is worthwhile to mention that bright white light emission was observed for all samples in the daytime. In Fig. 3, there are three characteristic emission peaks located at 483 (blue), 578 (yellow) and 667 nm (red), corresponding to $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$

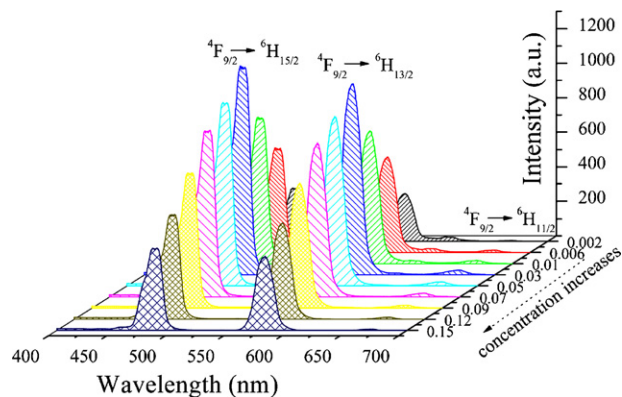


Fig. 3. Emission spectra of NaGdTiO₄ phosphors doped with various Dy³⁺ concentration under 281 nm excitation. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

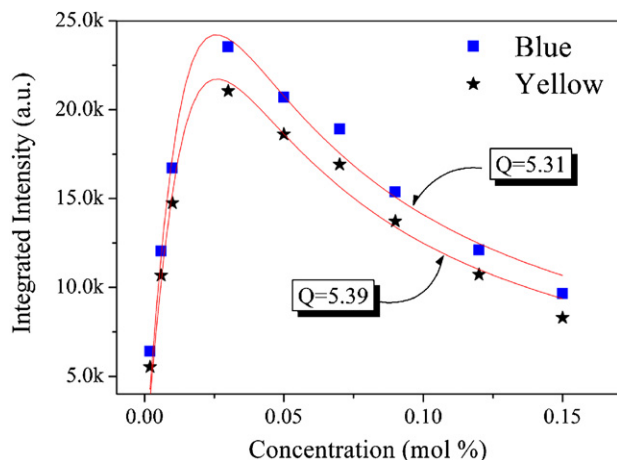


Fig. 4. Dependences of integrated intensities of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions on Dy^{3+} concentration. The solid squares and pentagrams are experimental data; the solid curves are the fitted curves.

and ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions of Dy^{3+} , respectively. The blue and the yellow ones are the two dominated emission peaks and they almost have the same intensity, thus white lights come from Dy^{3+} -doped $NaGdTiO_4$ can be seen by naked eyes. It is well known that the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition (blue) is a magnetically allowed transition, which can hardly be influenced by the crystal field environment around Dy^{3+} . The ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition (yellow) belongs to a forced electric dipole transition and can be easily disturbed by the crystal field environment. And if Dy^{3+} ions located at low symmetry sites with no inversion center, the yellow emission will be dominated in the emission spectra. In our studied samples, the intensity of the blue emission is a little stronger than that of the yellow one, indicating Dy^{3+} ions occupy the sites with high inversion symmetries in $NaGdTiO_4$. From Fig. 3, it can also be found that the profile of Dy^{3+} emission spectra was independent on Dy^{3+} concentration, which can be confirmed by the Y/B (the integrated emission intensity of ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) ratio kept constant (not shown here), implying that the crystal field environment around Dy^{3+} ions was not changed with the increase of Dy^{3+} concentration and only the emission intensity changed. When Dy^{3+} concentration reached 3 mol%, the fluorescence intensity reached the maximum value, however, which is still weaker than the commercial phosphor. Therefore, much more effort should be done to further improve the luminescence performance of $NaGdTiO_4:Dy^{3+}$ phosphor to meet its practical application in lighting area in the future.

3.3. Physical mechanism of energy transfer between Dy^{3+}

Fig. 4 shows the dependences of the integrated intensities of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (483 nm) and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (578 nm) transitions on Dy^{3+} concentration. The integrated intensities of the two emissions both increase with Dy^{3+} concentration firstly until Dy^{3+} concentration up to 3 mol%, and then decrease rapidly as Dy^{3+} concentration further increases. The optimal doping concentration of Dy^{3+} for obtaining the maximum luminescent intensity is 3 mol%.

Van Uitert has developed a model to explain the relationship between luminescent intensity and the doping concentration of luminescent centers. The model can be described as follows [22]:

$$I(C) = \frac{C}{k[1 + \beta C^{Q/3}]} \quad (1)$$

where C is the activator concentration, k and β are constants, Q means the interaction mechanism between RE ions. $Q=6, 8$ or 10 represent electric dipole–dipole ($D-D$), electric dipole–quadrupole

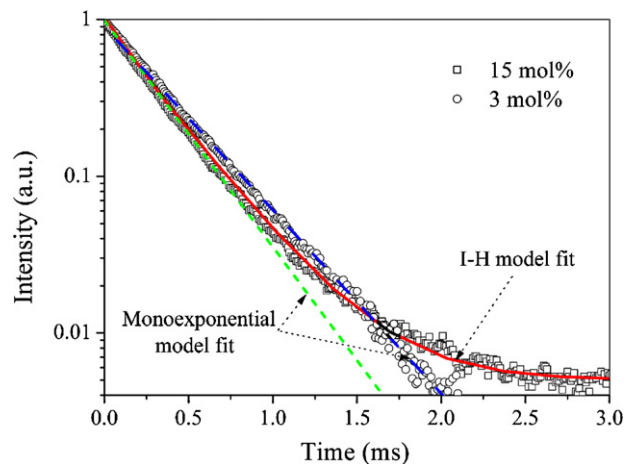


Fig. 5. Fluorescence decay curves of 3 and 15 mol% Dy^{3+} -doped $NaGdTiO_4$ phosphors. The open circles and squares are the experimental data, the solid and dashed curves are the fitted curves.

($D-Q$) or electric quadrupole–quadrupole ($Q-Q$) interaction, respectively. This equation was used to fit the experimental data in Fig. 4, the solid lines are the fitted results, the solid squares and pentagrams represent the experimental data. It can be seen that the experimental data can be fitted well by Eq. (1). The Q values for blue and yellow emissions are obtained from the fitting processes to be 5.31 and 5.39, which are close to theoretical value 6 for electric $D-D$ interaction. Therefore, we can conclude that the main interaction mechanism between Dy^{3+} ions in $NaGdTiO_4$ phosphors for concentration dependent fluorescence quenching of ${}^4F_{9/2}$ level is electric $D-D$ interaction.

With the increase of Dy^{3+} concentration, the distances between Dy^{3+} ions decreased. Thus, the probability of cross-relaxation (CR) between Dy^{3+} ions increased greatly, yielding depopulation of luminescent level. The possible CR channels had been described in previous report [23]. The Dy^{3+} ions at ${}^4F_{9/2}$ energy level may transfer their energy to Dy^{3+} ions at ground state and then de-excite to the possible levels (${}^6F_{9/2}, {}^6H_{7/2}$), (${}^6H_{9/2}, {}^6F_{11/2}$) or ${}^6F_{1/2}$, meanwhile make the Dy^{3+} ions at ground state elevated to the excited states ${}^6F_{3/2}, {}^6F_{5/2}$ or (${}^6H_{9/2}, {}^6F_{11/2}$).

Fig. 5 shows the fluorescence decay curves of ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission (578 nm) for 3 and 15 mol% Dy^{3+} -doped $NaGdTiO_4$ phosphors excited by 281 nm in a semi-logarithmic coordinate system. The open circles and squares represent the measured time decay curves for 3 and 15 mol% Dy^{3+} -doped samples, respectively. As can be seen from Fig. 5, at low doped concentration (3 mol%), the data can be well fitted by a monoexponential function. But the fluorescence decay data for 15 mol% Dy^{3+} -doped sample do not follow the monoexponential function, but exhibit a nonexponential behavior, which is caused by the energy transfer between Dy^{3+} ions. In this case, the fluorescence decay of donor can be expressed by I–H model which was developed by Inokuti and Hirayama based on the consideration of random distribution of luminescence centers in media. In the framework of I–H model, the donor's fluorescence decay fulfills the following nonexponential form in the case that electric multipole–multipole interaction between donor ions is dominant [24].

$$I(t) = I(0) \exp\left(\frac{-t}{\tau} - At^{3/s}\right) + f \quad (2)$$

where $I(0)$ is the intensity at the time $t=0$, τ is the radiative transition lifetime of Dy^{3+} in $NaGdTiO_4$, A is the nonradiative energy transfer factor, s has the same meaning as Q in Van Uitert's model. $s=6, 8, 10$ represent electric $D-D$, $D-Q$ or $Q-Q$ interaction, respectively. The fluorescence decay data for 15 mol% Dy^{3+} -doped

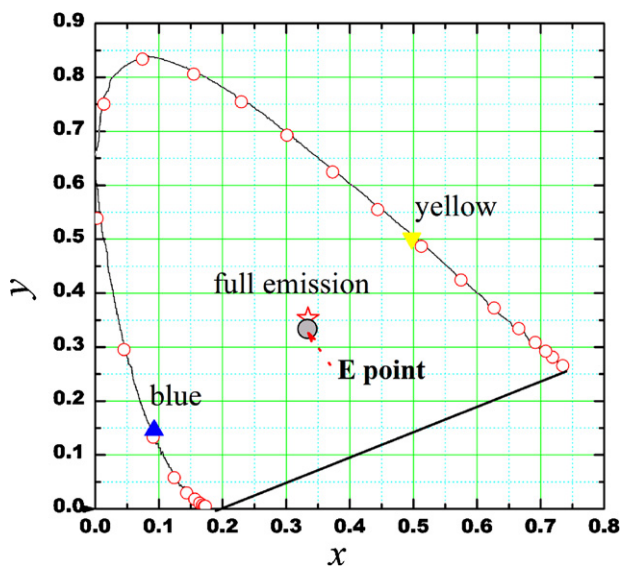


Fig. 6. The CIE color coordinates for Dy^{3+} -doped NaGdTiO_4 phosphors (open pentagram), and the color coordinates for solo blue and yellow emissions (solid triangles). (For interpretation of the references to color in the figure caption, the reader is referred to the web version of the article.)

NaGdTiO_4 can be fitted well by Eq. (2), and s value was found to be very close to the theoretical value of 6 for the electric $D-D$ interaction. This fact supports the conclusion derived from Van Uitert's model.

3.4. Colorimetric properties

The colorimetric property of a phosphor can be determined by the profile of its emission spectrum. Since the Y/B ratio does not change with Dy^{3+} ions concentration as mentioned in the above analysis in Section 3.2, it can be sure that the color coordinates of the studied phosphors will not change with Dy^{3+} concentration. The Commission International De I-Eclairage (CIE) color coordinates for all of the Dy^{3+} -doped NaGdTiO_4 phosphors were calculated and all of them almost have the same color coordinates. The average values of color coordinates are calculated to be $x=0.3345$, $y=0.3535$. Additionally, the color coordinates for solo blue and yellow emissions were also calculated in the same way. These color coordinates are shown in Fig. 6. It can be seen that the straight line decided by the two points of the color coordinate sites for blue and yellow

emissions just crosses the E point (Energy Equal Point) whose color coordinates are $x=y=0.3333$. This fact says that white light could be achieved by combining blue and yellow emissions if their intensity ratio is proper, which can be confirmed by our experiments. It should be mentioned that although the color coordinates for the studied phosphors are very close to the E point, the quality of the obtained white light is still not ideal since the lack of green and red components in the emission spectra of the studied phosphors. Nevertheless, this phosphor can be one of the candidate phosphors to co-work with the other green and red ones for realizing polychrome lighting source with excellent color rendering index.

3.5. Thermal quenching properties

Thermal stability of luminescence (TSL) is one of the important properties of phosphors. The TSL means that the luminescence intensity of the phosphor may change dramatically with increasing temperature. To evaluate the TSL property of Dy^{3+} -doped NaGdTiO_4 phosphors, the emission spectra of 3 and 15 mol% Dy^{3+} -doped samples were measured at various temperatures from room temperature to 633 K excited by 281 nm UV light. Similar variation trend of luminescence intensity with temperature was observed. The luminescence spectra of 3 mol% Dy^{3+} -doped sample measured at different temperatures as a representative are depicted in Fig. 7. As can be seen, with the increase of temperature the emission intensities for all emissions of Dy^{3+} ions decrease. In addition, it should be noted that a new peak located at 456 nm corresponding to the ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ transition, is clearly observed at higher sample temperatures (the one measured at 453 K as an example is shown in the inset of Fig. 7), and its intensity increases with the increase of the sample temperature. The energy difference between ${}^4\text{F}_{9/2}$ and ${}^4\text{I}_{15/2}$ levels is small (about 1000 cm^{-1}) and the populations of ${}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2}$ levels fulfill Boltzmann's distribution at a certain temperature, thus ${}^4\text{I}_{15/2}$ level can be thermally populated easily by ${}^4\text{F}_{9/2}$ level at higher temperature, yielding the increase in intensity of 456 nm emission as the sample temperature increases. Fig. 8 shows the temperature dependence of integrated emission intensity ratio of ${}^4\text{I}_{15/2} \rightarrow {}^6\text{H}_{15/2}$ to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ of 3 and 15 mol% Dy^{3+} -doped samples excited by 281 nm UV light, which can be described by the following equation on the basis of Boltzmann's distribution law [25]:

$$\frac{I_{4\text{I}_{15/2}}}{I_{4\text{F}_{9/2}}} = ae^{-\Delta E/kT} \quad (3)$$

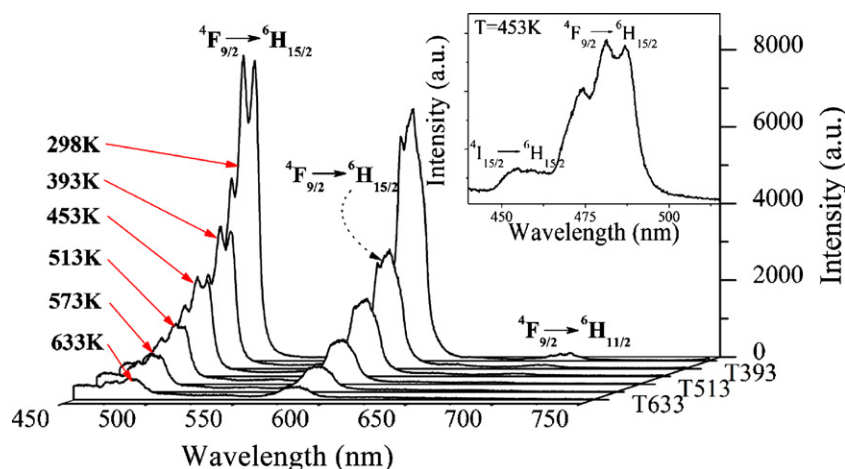


Fig. 7. Temperature (298–633 K) dependences of luminescence spectra of 3 mol% Dy^{3+} -doped NaGdTiO_4 phosphor excited by 281 nm. The inset shows the emission spectrum in blue region measured at 453 K.

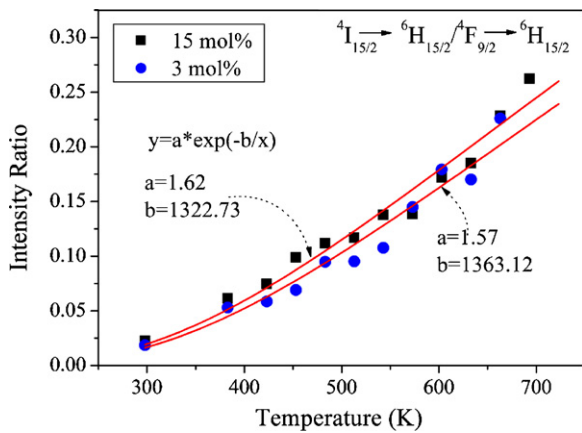


Fig. 8. Temperature dependences of integrated emission intensity ratio of ${}^4I_{15/2} \rightarrow {}^6H_{15/2}$ to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions for 3 and 15 mol% Dy^{3+} -doped samples. The solid dots represent the experimental data, the solid lines are the fitted curves.

where ΔE is the energy difference between ${}^4F_{9/2}$ and ${}^4I_{15/2}$ levels, k is Boltzmann's constant, a is a constant independent from temperature. Eq. (3) was used to fit the experimental data in Fig. 8. As can be seen from Fig. 8, the measured intensity ratio can be fitted well by Eq. (3). The temperature dependent behavior of fluorescence intensity ratio (FIR) of Dy^{3+} indicates that Dy^{3+} -doped $NaGdTlO_4$ phosphor may be a good optical temperature sensor material which is similar to those reported in Refs. [26,27], where two green upconversion emissions from ${}^2H_{11/2}$ and ${}^4S_{3/2}$ to ${}^4I_{15/2}$ of Er^{3+} were used as a temperature indicator. Furthermore, ${}^4I_{15/2} \rightarrow {}^6H_{15/2}$ transition can be observed at higher temperature and the $NaGdTlO_4$ is more stable, thus Dy^{3+} -doped $NaGdTlO_4$ may be a good candidate material for high temperature sensing device.

In general, luminescence intensity decreases with an increase of temperature [28,29]. It is known that the luminescent ion can reach the ground state via several pathways, such as cascade multiphonon relaxation, energy transfer from the luminescent level and crossover effect, etc. [22,30,31]. To better understand the temperature quenching behavior, the fluorescence decays of 578 nm emission for 3 and 15 mol% Dy^{3+} -doped $NaGdTlO_4$ phosphors were measured at various temperatures excited by 281 nm. The initial-intensity-normalized fluorescent decay curves of 3 mol% Dy^{3+} -doped sample as a representative are plotted in a semi-logarithmic coordinate system as shown in Fig. 9. It can be seen that the fluorescence decay curves are almost not changed with temperature. Each fluorescence decay curve can be fitted well with

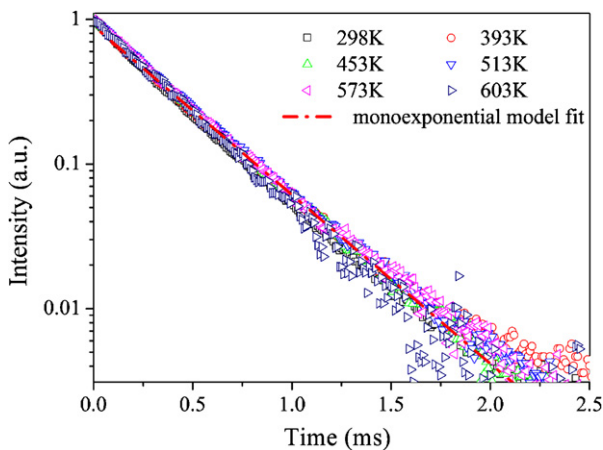


Fig. 9. Fluorescence decays of ${}^4F_{9/2}$ energy level for 3 mol% Dy^{3+} -doped sample measured at various temperatures.

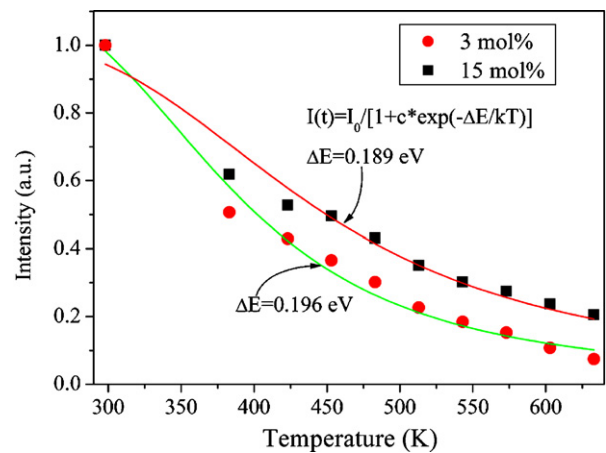


Fig. 10. Temperature dependence of the integrated emission intensity of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of 3 and 15 mol% Dy^{3+} -doped $NaGdTlO_4$ phosphors excited by 281 nm.

the same monoexponential function, indicating that the cascade multiphonon relaxation process can be neglected even at high temperature. It should be mentioned that for the sample doped with 15 mol% Dy^{3+} , the fluorescence decay curves do not change with temperature yet and follow the same nonexponential function as discussed in Section 3.3, indicating energy transfer behavior does not change with temperature. Therefore, we deduce that the energy transfer processes are not responsible for the temperature quenching of ${}^4F_{9/2}$ level of Dy^{3+} , either.

After excluding the above two possible mechanisms of fluorescence temperature quenching, the crossover process should be checked to find the physical nature of temperature dependent fluorescence quenching of Dy^{3+} . Besides, it has been widely observed and extensively studied in Eu^{3+} -doped luminescent materials [29,32–34]. In fact, the crossover quenching is a thermal activation process in which the relationship between luminescence intensity and sample temperature can be described as the following equation [35]:

$$I(T) = \frac{I_0}{1 + ce^{-\Delta E/kT}} \quad (4)$$

where I_0 is the initial luminescent intensity, $I(T)$ is the luminescent intensity at temperature T , c is a constant, k is Boltzmann's constant, and ΔE is an activation energy for an electron at excited state to overcome the potential barrier and reach other states. In order to study the temperature quenching process of Dy^{3+} ions in $NaGdTlO_4$ phosphors, the dependences of integrated luminescence intensity of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition on temperature for both of the samples doped with 3 and 15 mol% Dy^{3+} ions were obtained from the temperature-dependent emission spectra and are shown in Fig. 10. Eq. (4) was used to fit the experimental data in Fig. 10, and it is found that the experimental data are fitted well by Eq. (4). In fitting processes, the activation energies ΔE were obtained to be 0.20 and 0.19 eV for 3 and 15 mol% Dy^{3+} -doped sample, respectively. It should be noted that the activation energies for these two samples are very similar. This fact implies that the crossover effect is the main mechanism for the temperature quenching of Dy^{3+} fluorescence.

4. Conclusions

Dy^{3+} -doped $NaGdTlO_4$ phosphors were successfully synthesized by a solid-state reaction method. The crystal structure of the resultants was characterized by means of XRD. From spectroscopic studies, it was found that the energy transfer from host

NaGdTiO₄ to doping Dy³⁺ is very efficient, and intense blue and yellow emissions can be obtained upon UV excitation corresponding to the host absorption band. Chromatic analysis on the phosphors indicates that white light could be achieved from the Dy³⁺-doped NaGdTiO₄ phosphors. Based on the I–H and Van Uitert's models, the electric dipole–dipole interaction was confirmed to be the physical mechanism for the energy transfer between Dy³⁺ ions. From the measurements and analysis on the fluorescence decays and temperature-dependent emission spectra, it was also found that the crossover process is the physical nature of fluorescence temperature quenching of Dy³⁺ ions in NaGdTiO₄ phosphors.

Acknowledgments

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