Influence of Si^{4+} substitution on the temperature-dependent characteristics of $Y_3Al_5O_{12}$:Ce*

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A series of $Y_3Al_5O_{12}$:Ce (YAG:Ce) phosphors doped with different Si^{4+} concentrations is prepared by solid-state reaction. The temperature dependent characteristics of luminescent spectrum and decay time of Ce^{3+} are investigated. With Si^{4+} doped, the emission spectrum shows a blue shift due to a decrease of the splitting of 5d levels of Ce^{3+} ion. The thermal stability is greatly improved by adding Si^{4+} because the activation energy ΔE increases from 0.1836 eV to 0.2401 eV. The study of the decay times against temperature for various doping concentrations of Si^{4+} shows that the calculated nonradiative decay rate is affected by Si^{4+} substitution. The results are explained by the configurational coordinate diagram.

Keywords: phosphor, luminescence, temperature dependence, decay time

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1. Introduction

Owing to excellent properties such as high efficiency low power consumption, better reliability, long lifetime white light-emitting diodes (LEDs) are considered as the next generation of solid-state lighting sources.[1,2] White light emission can be achieved by multi-chip LEDs or a combination of chip and phosphor. For the second method, the temperature around chip will be quite high when the chip works This can result in the thermal quenching of the phosphor coated on the chip and the restriction on the application of the equipment It is urgently desired to achieve good quenching properties of phosphors for demand of application

In recent years, the behaviours of phosphors at different temperatures were studied by several groups. Kim *et al.*[3] investigated the temperature dependence of emission spectrum of full-colour emitting $Ba_3MgSi_2O_8$:Eu^{2+}, Mn^{2+}. They reported that the nonradiative transition probability was strongly related to temperature. With the temperature increasing, the three emission peaks of $Ba_3MgSi_2O_8$:Eu^{2+}, Mn^{2+} each showed a blueshift with intensity decreasing. The fluorescence quench was realized from enhanced phonon–electron interaction and increased nonradiative transitions probability. They further owed the blueshift behaviours with temperature increasing to the appearing of the anti-Stokes effect by the assistance of thermally active phonon. Temperature dependent decay time of La_2O_2S:Tb was studied over a low temperature range 5–60 °C by Yap *et al.*[4] The decay time of phosphor decreased with temperature at lower Tb concentration The thermal quenching of Tb in La_2O_2S was ascribed to the CTS crossover relaxation to Frank–Condon shifted states. However opposite trend of decay time for higher doping concentration was observed to be due to the change of crystal structure.

The change of host structure, caused by ions doping, can affect the optical properties of material. It was reported that[5] the replacement of Sr^{2+} by a small quantity of Ca^{2+} in $Sr_2Si_5N_8$:Eu^{2+} could cause an increase of the Stokes shift which led to a significant red-emission shift. Niittykoski *et al.*[6] revealed that substitution of Al^{3+} by B^{3+} in $SrAl_2O_4$:Eu^{2+} would cause the thermoluminescence peaks to shift towards lower temperature and the intensity to decrease with the increase of B^{3+} doping concentration. Both the trap concentration and the depth of trap level thus

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decreased, resulting in the weakening of the persistent luminescence with the increase of B^{3+} doping concentration.

In the present paper, Si^{4+} ions are chosen as substitution into YAG:Ce phosphors. A series of $Y_{2.94}(Al_{5-x}Si_x)O_{12}$:$Ce_{0.06}$ is prepared by a solid-state reaction. By discussing the influence of Si^{4+} doping on energy level structure of rare earth ions in YAG:Ce phosphors, we investigate the effect of Si^{4+} substitution on luminescence spectrum and the temperature dependent decay time characteristics.

2. Experiment

The phosphors were prepared by the solid-state reaction according to the formula $Y_{2.94}(Al_{5-x}Si_x)O_{12}$:$Ce_{0.06}$ where x = 0, 0.26, 0.66 and 1.06. The starting materials were milled completely and then sintered in an aluminum crucible at 1500 °C for several hours in a reducing ambient.

X-ray power diffraction (XRD) patterns were characterized on a Rigaku 2500/PC x-ray diffractometer with using a Cu Kα radiation source (1.542 Å) (1 Å=0.1 nm) at 40 kV and 150 mA. Photoluminescence (PL) spectra and fluorescence decay spectra were recorded by Jobin Yvon FL3-221-TCSPC fluorescence spectrophotometer with using a 450W xenon lamp and a 340 nm NanoLED with max repetition rate 1MHz as the excitation sources respectively.

3. Results and discussion

Figure 1 shows the XRD patterns of YAG:Ce with different Si^{4+} dopings. The diffraction peaks of the as-synthesized samples with 0, 0.26, 0.66 mol of Si^{4+} doping match very well with the JCPDF files (No. 79-1892 of YAG), belong to the cubic lattice structure. But two additional peaks (indicated by $*$ in Fig. 1) are observed when the doping quantity of Si^{4+} increases to 1.06 mol. According to the standard JCPDF files, the additional phase structure corresponds probably to $Y_2Si_2O_7$.

The influence of concentration of Si^{4+} addition on YAG:Ce emission spectrum (excited at 460 nm) is shown in Fig. 2. The emission peak shifts towards higher energies with Si^{4+} concentration increasing. The phenomenon can be explained by the configurational coordinate diagrams shown in Fig. 3.

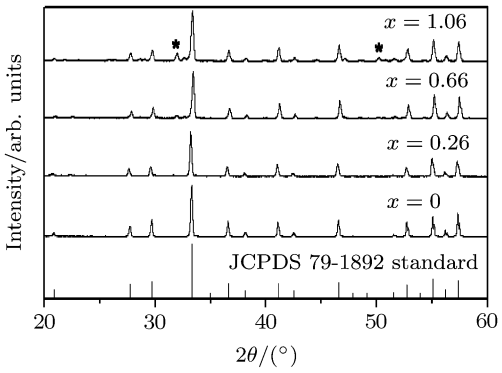


Fig. 1. XRD patterns of $Y_{2.94}(Al_{5-x}Si_x)O_{12}$:$Ce_{0.06}$.

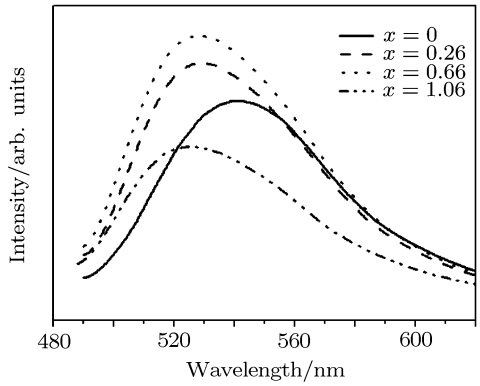


Fig. 2. Emission spectra of $Y_{2.94}(Al_{5-x}Si_x)O_{12}$:$Ce_{0.06}$ x = 0, 0.26, 0.66, 1.06 mol.

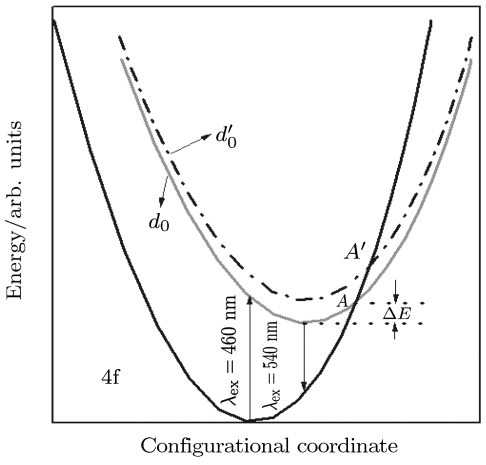


Fig. 3. Configurational coordinate diagram of YAG:Ce, where d_0 and d'_0 denote the lowest excited state energy level of 5d before and after Si^{4+} doped, respectively.

By using Ce^{3+} to replace Y^{3+} ions surrounded with eight oxygen atoms in YAG, slightly larger ionic radius of Ce^{3+} substitution than that of Y^{3+} will result in the spitting of 5d levels of Ce^{3+} due to distortion of crystal lattice.[7] A similar situation in crystal

lattice but with compression of the cubelike structure also happens to the replacement of Al^{3+} by Si^{4+} because the ionic radius of Si^{4+} is slightly smaller than that of Al^{3+}. As a result, the weakened distortion around Ce^{3+} ion by Si^{4+} doping reduces the splitting of 5d levels of Ce^{3+} ion. The energy gap between lowest 5d level and the top of 4f level becomes wide, which indicates the blue shift of emission peak wavelength as shown in Fig. 2.

Figure 2 also displays emission intensity enhancement as Si^{4+} concentration increases. The intensity reaches a maximum when the Si^{4+} concentration comes to 0.66 mol and then diminishes with Si^{4+} content increasing further. Activation energy is a very important parameter characterizing the relaxation of electrons between two levels. For the case of higher Si^{4+} addition, the blue shift of emission peak implies that the splitting of 5d state becomes weak. That results in increased activation energy and lower possibility of nonradiative transitions.[8] But an additional phase will appear with higher Si^{4+} concentration (shown in Fig. 1), resulting in the quenching of luminescence.

To clearly ascertain the activation energy and the thermal stability of Si^{4+} doped and undoped YAG:Ce, the temperature dependences of PL spectrum are measured in a temperature range from room temperature (RT) to 553 K under the excitation at 460 nm. The temperature-dependent emission spectra of YAG:Ce phosphor with no Si^{4+} added and 0.26 mol Si^{4+} added are shown in Figs. 4(a) and 4(b), respectively.

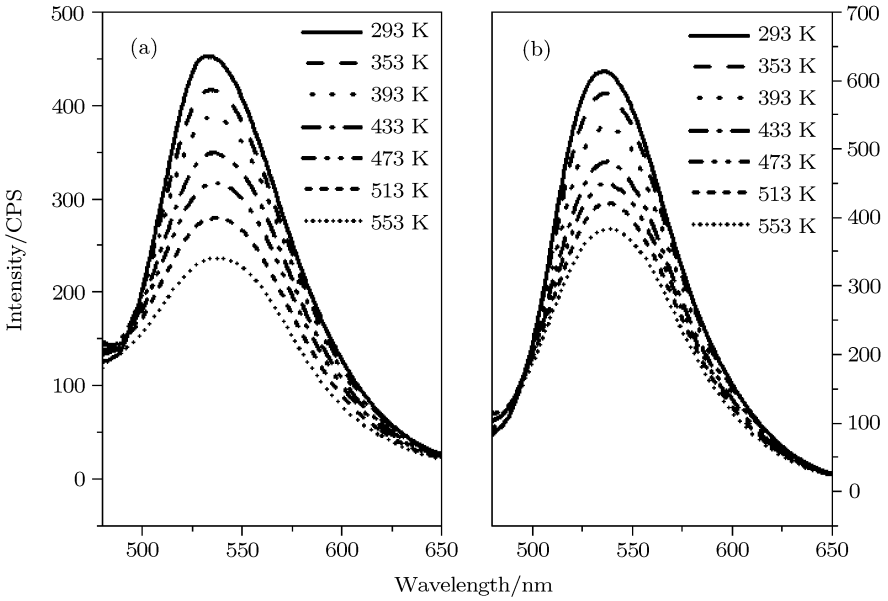


Fig. 4. Emission spectra excited at 460 nm of $Y_{2.94}(Al_{5-x}Si_x)O_{12}$:$Ce_{0.06}$ under various temperatures and $x = 0$ (a) and 0.26 mol (b).

With temperature increasing from RT up to 553 K, the luminous intensity of the undoped phosphor drops by 47.8%, and by 37.4% for sample with 0.26 mol Si^{4+} concentration. The temperature dependence of luminescent intensity can be described by the following formula:[9]

$$I(T) = \frac{I(0)}{1 + A\exp(-\Delta E/kT)}, \tag{1}$$

where T is the absolute temperature, A is a constant, $I(0)$ corresponds to the emission intensity at absolute temperature, ΔE is the activation energy for thermal quenching process, and k is the Boltzmann constant.

When the obtained thermal energy E of electron on excited level is higher than the activation energy ΔE, the electron will be transferred to ground state at the crossing point between the excited state and the ground state via nonradiative transition. The quench of emission intensity corresponding to temperature will happen. From the temperature-dependent emission spectra of samples with different Si^{4+} concentrations, the parameters in formula (1) are fitted and shown in Table 1. It can be noticed obviously that the activation energy ΔE increases with Si^{4+} content in-

creasing which accords with the result from the previous configurational coordinate diagrams. As a result, the decline of emission intensity is improved with temperature rising for high concentration Si^{4+} doping.

Table 1. Correlative parameters of $Y_{2.94}(Al_{5-x}Si_x)O_{12}$:$Ce_{0.06}$ phosphors in formula (1).

parameter / x/mol	$I(0)$	A	ΔE/eV
$x = 0$	1.024	121.80	0.1836
$x = 0.26$	1.025	145.50	0.2284
$x = 0.66$	1.006	137.06	0.2356
$x = 1.06$	1.009	176.09	0.2401

The luminescent decay spectrum can be regarded as an important method of studying the luminous performance of phosphors because it is reliable for identification of interaction on rare earth ions by crystal lattice exquisitely. For direct effects of temperature on thermal-phonon energy and on transition possibility of luminescent centers, the decay times of luminescent centres at different temperatures are considered to be due to the thermal quenching mechanism.

Figure 5 shows the temperature dependences of decay time of Ce^{3+} for different Si^{4+} doping concentrations of YAG:Ce and the inset displays experimental decay curves with 0.26 mol Si^{4+} doping at different temperatures. The fitted results match with single exponential decay law. It can be seen that the decay time becomes shorter with temperature increasing as indicated in Fig. 5. For example, the decay time of phosphor with 0.26 mol Si^{4+} at 300 K is 62.59 ns, whilst down to 47.96 ns at 513 K.

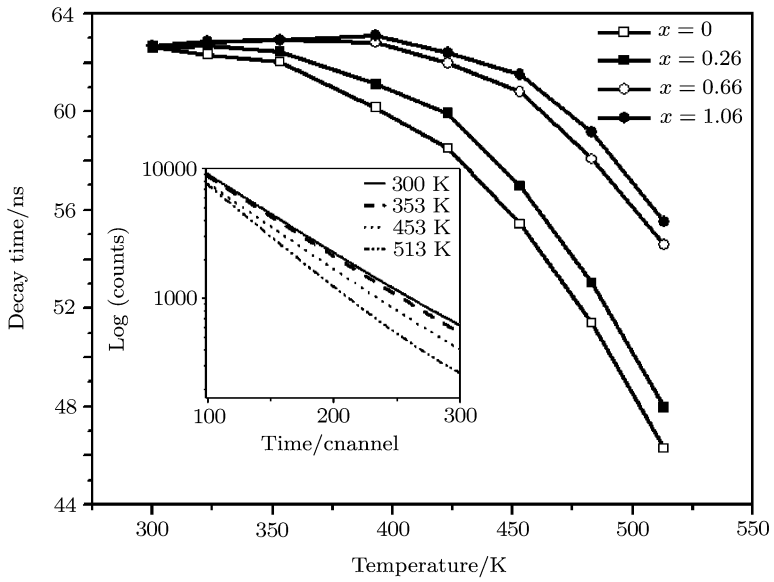


Fig. 5. Decay times against temperature for various dopant concentrations of Si^{4+}, where the inset displays luminescent intensity decaying with temperature.

The decay time contains the contributions from radiative and nonradiative process. With temperature increasing, the nonradiative process will dominate.[10] The relationship among the nonradiative decay rate, the activation energy and temperature follows the Arrhenius law:[11]

$$W_{\rm NR} = \tau_0^{-1} \exp(-\Delta E/kT), \qquad (2)$$

where k is the Boltzmann constant, ΔE is the activation energy, and τ_0 is the decay time when T tends to infinity. For the 5d–4f transitions of Ce^{3+}, τ_0 is regarded as a constant. As the temperature increases, the nonradiative transition rate increases accompanied with decay time decreasing.

The doping concentration also influences the decay time of luminescent centres of phosphors. Figure 5 also illustrates that the decay slows down with Si^{4+} concentration increasing. For discrete luminescence of Ce^{3+} in YAG, the shift of excited state of Ce^{3+} ion influences the fluorescence lifetime. With Si^{4+} doping concentration increasing, lowest 5d level of Ce^{3+} shifts to high energies, and the activation energy ΔE and nonradiative decay rate $W_{\rm NR}$ show their reverse trends.

4. Conclusion

YAG:Ce phosphors doped with Si^{4+} are synthesized via solid-state reaction. Partial substitution of Al^{3+} ions by Si^{4+} of YAG:Ce is suggested to modulate the splitting of energy level of Ce^{3+}. From experimental blue shift of the emission spectrum, we conclude that Si^{4+} substitution reduces the splitting of 5d levels and elevates the lowest excited state energy level of 5d. The thermal stability is improved with Si^{4+} added because the activation energy ΔE increases. The decay time of phosphor decreases with temperature rising due to the increase of nonradiative transition rate, which is explained by the Arrhenius law.

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