Energy Transfer Behavior and Color-Tunable Properties of $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{RE}^{3+}$ ($\text{RE}^{3+} = \text{Tm}^{3+}, \text{Dy}^{3+}, \text{Tm}^{3+}/\text{Dy}^{3+}$) for White-Emitting Phosphors

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$\text{Tm}^{3+}/\text{Dy}^{3+}$ -codoped $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors have been synthesized using a high-temperature solid-state reaction method. The crystal structure, x-ray diffraction patterns, and photoluminescence (PL) properties of the rare-earth (RE) ions, and energy transfer (ET) processes between RE ions, were investigated in detail. The quenching concentration of Tm^{3+} and Dy^{3+} singly doped in $\text{Ca}_2\text{Al}_2\text{SiO}_7$ was determined to be 0.006 mol and 0.02 mol, respectively. Under excitation at 357 nm, $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tm}^{3+}$ phosphors showed emission lines of Tm^{3+} corresponding to $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transitions. Efficient ET from Tm^{3+} to Dy^{3+} ions was observed, leading to color-tunable emissions of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},x\text{Dy}^{3+}$ ($x = 0$ mol to 0.02 mol) phosphors. Theoretical calculations revealed that the efficiency of the ET gradually increased with increase in the Dy^{3+} ion concentration, reaching a maximum of $\sim 42.1\%$ at Tm^{3+} ion concentration of 0.006 mol. Furthermore, at 473 K, the quantum efficiency was calculated to be 79.8% at room temperature, confirming the good thermal stability of the $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},x\text{Dy}^{3+}$ phosphors.

Key words: Fluorescence spectrum, $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tm}^{3+}/\text{Dy}^{3+}$, energy transfer, thermal stability

INTRODUCTION

Solid-state lighting devices based on inorganic white light-emitting diode (w-LEDs) have attracted considerable interest owing to their robustness, environmental friendliness, and energy-saving features, and can be regarded as a replacement for traditional incandescent and fluorescent lamps.^{1,2} Currently, two methods to realize white light with LEDs have become popular. The first involves combining tricolor (red, blue, and green) phosphors

under near-ultraviolet (NUV) excitation.³ This method yields lamps with better color rendition,² and addition of a yellow-emitting phosphor improves the color rendition index (CRI) further. Recently, much progress has been made in the emission efficiency of LED chips in the near-UV to deep-blue range.^{4–6} However, in terms of cost and light output, near-UV chips remain greatly inferior to blue chips. Thus, the second approach, which is considered more practical, involves coating excitable blue, green, and red phosphors on a blue chip.^{3–5} Therefore, it is necessary to find novel phosphors with remarkable properties under near-

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UV excitation, such as high quantum efficiency (QE) and small thermal quenching.

Several single-component phosphors for use in UV-pumped w-LEDs have been reported, including $\text{Sr}_3\text{Y}(\text{PO}_4)_3:\text{Eu}^{2+}, \text{Mn}^{2+}$,⁷ $\text{Ba}_2\text{Ca}(\text{BO}_3)_2:\text{Ce}^{3+}, \text{Mn}^{2+}$,⁸ $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}, \text{Tb}^{3+}$,⁹ and $\text{Sr}_3\text{B}_2\text{O}_6:\text{Ce}^{3+}, \text{Eu}^{2+}$.¹⁰ However, these phosphors were synthesized in a reducing atmosphere, which may also limit their further applications owing to the complex preparation process. Thus, development of novel single-component white light-emitting phosphors that could be synthesized under ambient atmospheric conditions is highly desirable.

Most rare-earth ions with rich energy levels, which are regarded as the most popular activators, have been prepared under ambient atmospheric conditions. They can exhibit various emissions over the ultraviolet–visible–near infrared (UV–Vis–NIR) spectral region via f – f or d – f transitions. Dy^{3+} is one of the most common rare-earth ions that play a major role in production of different types of light-emitting material, as it exhibits intense emissions in the blue and yellow regions, attributed to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transitions, respectively.^{10,11} However, the quality of the resulting white light is unsatisfactory, as the color coordinates of the Dy^{3+} phosphor are quite far from the equal energy point. For several Dy^{3+} -doped phosphors, the intensity of the yellow light emission is stronger than that of blue light emission; the mixed color therefore forms just stable yellow light. To obtain white light, it may be more feasible to dope Dy^{3+} phosphors with other rare-earth ions,^{12–15} as exemplified by $\text{Gd}_2(\text{MoO}_4)_3:\text{Dy}^{3+}/\text{Eu}^{3+}$,¹² $\text{Sr}_3\text{MgSi}_2\text{O}_8:\text{Dy}^{3+}/\text{Ce}^{3+}$,¹³ $\text{Ba}_2\text{MgSi}_2\text{O}_7:\text{Dy}^{3+}/\text{Eu}^{2+}$,¹⁴ and $\text{NaGdTiO}_4:\text{Dy}^{3+}/\text{Sm}^{3+}$.¹⁵ Moreover, the color coordinates of such phosphors can be modulated by codoping with Tm^{3+} ; indeed, $\text{BaY}_2\text{Si}_3\text{O}_{10}:\text{Tm}^{3+}/\text{Dy}^{3+}$,¹⁶ $\text{KSr}_4(\text{BO}_3)_3:\text{Tm}^{3+}/\text{Dy}^{3+}$,¹⁷ and $\text{Ca}_9\text{Y}(\text{PO}_4)_7:\text{Tm}^{3+}/\text{Dy}^{3+}$ ¹⁸ single-phase white-light-emitting phosphors have been reported. Because, under UV excitation, Tm^{3+} -doped materials can emit in the blue light region owing to the $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition, Tm^{3+} ions are generally introduced to adjust the ratio of yellow to blue emission, which has helped researchers to obtain white light with enhanced color purity.^{10,19,20} Furthermore, the ET process between Tm^{3+} and Dy^{3+} ions can occur, leading to white light emission from $\text{Tm}^{3+}/\text{Dy}^{3+}$ -codoped compounds. In recent years, record luminance values with output QE of about $\sim 90\%$ have been realized using several host lattices.²¹ To the best of the authors' knowledge, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ is an excellent host for phosphors owing to its good physical and chemical stability, confirming its potential for application in LEDs. Although impressive work has been done with regard to $\text{Tm}^{3+}/\text{Dy}^{3+}$ -codoped phosphors, further modulation of the color coordinates of such phosphors by codoping $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tm}^{3+}, \text{Dy}^{3+}$ has not yet been investigated, to the best of the authors' knowledge.¹⁷ In

this study, the photoluminescence (PL) characteristics and temperature-dependent luminescent properties of the obtained phosphors as well as the ET mechanism of Tm^{3+} - and Dy^{3+} -activated $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors were investigated. The results suggest that $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, x\text{Dy}^{3+}$ might be used as a potential single-phase phosphor system for UV-based w-LEDs.

EXPERIMENTAL PROCEDURES

Synthesis

A series of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}$, $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.02\text{Dy}^{3+}$, and $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, x\text{Dy}^{3+}$ ($x = 0.01, 0.015, 0.02$) samples were prepared by conventional solid-state reaction at high temperature. High-purity Dy_2O_3 (99.99%) and Tm_2O_3 (99.99%), analytical-purity CaCO_3 , Al_2O_3 , and H_3SiO_3 were used as starting materials. Stoichiometric amounts of the above precursors were ground well and placed into an alumina crucible, then heated at 900°C for 2 h and sintered at 1300°C for 2 h.

Characterization

The phase purity of all the obtained samples was ascertained by x-ray diffraction (XRD) measurements using a Rigaku D/max-II B x-ray diffractometer at scan rate of $10^\circ/\text{min}$ in the 2θ range from 10° to 80° . The particle size and morphology of the phosphors were observed by field-emission scanning electron microscopy (FESEM) using a Zeiss SUPRA 55VP microscope operated at acceleration voltage of 20 kV. Photoluminescence excitation (PLE) and emission spectra were monitored using an Edinburgh Instruments FLS920 spectrofluorometer with a continuous 450-W xenon lamp as excitation source and R928 photomultiplier tube as detector. Temperature-dependent PL spectra were recorded using the same spectrophotometer and detectors. Luminescence decay time curves were collected using a xenon lamp (μF920H , 200 nm to 900 nm, 10 Hz to 100 Hz) with the same spectrophotometer and detectors.

RESULTS AND DISCUSSION

The powder XRD patterns of the $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}$, $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.02\text{Dy}^{3+}$, and $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, x\text{Dy}^{3+}$ ($x = 0.01, 0.015, 0.02$) phosphors are shown in Fig. 1a, revealing that all the diffraction peaks are in good agreement with that of phase-pure $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (PDF#87-0969). Introduction of Tm^{3+} and Dy^{3+} did not change the phase. $\text{Ca}_2\text{Al}_2\text{SiO}_7$ crystallized in a tetragonal crystal system in space group $P4_21$ m with lattice parameters of the unit cell of $a = b = 0.7687$ nm and $c = 0.5065$ nm, and interplanar spacing (d) of 0.2844 nm. The crystal structure contains three distinct sites for occupation by cations: an eightfold-coordinated site called the Thomson cube (TC)

occupied by Ca^{2+} ions, a regular tetrahedral site (T_1) entirely occupied by Al^{3+} ions, and a highly distorted tetrahedral site (T_2) at which Si^{4+} and Al^{3+} ions were statistically distributed (Fig. 1b). The effective ionic radii r of the cations with different coordination numbers (CNs) reported by Shannon^{21,22} suggest that Tm^{3+} and Dy^{3+} ions should occupy Ca^{2+} sites preferably, because the ionic radii of Dy^{3+} ($r = 1.03 \text{ \AA}$ for CN = 8) and Tm^{3+} ($r = 1.05 \text{ \AA}$ for CN = 8) are close to that of Ca^{2+} ($r = 1.12 \text{ \AA}$ for CN = 8).¹⁸ As both four-coordinated Si^{4+} ($r = 0.26 \text{ \AA}$) and Al^{3+} ($r = 0.39 \text{ \AA}$) sites are relatively too small for occupation by Tm^{3+} and Dy^{3+} , it can be concluded that Tm^{3+} and Dy^{3+} will tend to prefer to occupy Ca^{2+} rather than Si^{4+} and Al^{3+} sites. FESEM was carried out to provide information regarding the surface morphology, shape, and grain size of the synthesized phosphors. The morphology of the synthesized $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, 0.02\text{Dy}^{3+}$ phosphor was also observed by FESEM (Fig. 2a, b). These images show that the surface of the $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, 0.02\text{Dy}^{3+}$ phosphor was irregular, indicating an inhomogeneous distribution of crystallite sizes.

Figure 3a shows the PLE and PL spectra of the Dy^{3+} -activated $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phases. It can be seen that the excitation spectrum monitored at emission wavelength of 580 nm contained an absorption band ranging from 300 nm to 500 nm. The emission spectrum ($\lambda_{\text{ex}} = 350 \text{ nm}$) consisted of bands centered at 480 nm, 532 nm, 580 nm, and 653 nm, attributed to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_9/2 + ^6\text{F}_{11/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$, and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$ transitions of the Dy^{3+} ion, respectively. Figure 8 shows a representative energy level diagram that illustrates the luminescence mechanism of the $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$ phosphors.

The quenching concentration of Dy^{3+} ions in $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$ was found to be 0.02 mol (Fig. 3a, inset). Furthermore, from the emission spectrum, it can be seen that the intensity of the yellow light emission peak of the $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$ phosphor was stronger than that of the blue light emission peak, suggesting that the host lattice should be codoped with blue light-emitting ions to improve the color coordinates. The PLE and PL spectra of the Tm^{3+} -activated $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors are shown in Fig. 3b. The excitation spectrum ($\lambda_{\text{em}} = 455 \text{ nm}$) consisted of a main peak centered at 357 nm, corresponding to the transition from the $^3\text{H}_6$ ground state to the $^1\text{D}_2$ excited state of Tm^{3+} . The emission spectrum recorded under excitation at wavelength of 357 nm exhibited a strong emission peak centered at 455 nm and a weak emission band at 478 nm, corresponding to the $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition, respectively.²³ The emission mechanism for the Tm^{3+} ions in the $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phase is presented in the partial energy level diagram shown in Fig. 8. The PL emission intensity increased with the Tm^{3+} ion concentration, reaching saturation at $x = 0.006$, after which the emission

Fig. 1. (a) XRD patterns of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}$, $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.02\text{Dy}^{3+}$, and $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, x\text{Dy}^{3+}$ ($x = 0$ to 0.02), (b) crystal structure of $\text{Ca}_2\text{Al}_2\text{SiO}_7$ with $[\text{SiO}_4]$ polyhedrons viewed along c -axis direction.

intensity decreased with further increase of the concentration owing to the concentration quenching effect (Fig. 3b, inset).

Figure 4 displays the excitation spectra of the $\text{Ca}_2\text{Al}_2\text{SiO}_7$ sample, revealing the Tm^{3+} and Dy^{3+} emission at $\lambda_{\text{em}} = 455 \text{ nm}$ and $\lambda_{\text{em}} = 580 \text{ nm}$ at room temperature. For the Tm^{3+} -doped sample, the main excitation peak occurred at 357 nm, which can be assigned to the $\text{Tm}^{3+}: ^3\text{H}_6 \rightarrow ^1\text{D}_2$ transition monitored at 455 nm. The excitation spectrum of the 580-nm emission (where Tm^{3+} does not emit) shows the well-known Dy^{3+} bands at around 290 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{D}_{7/2}$), 325 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{I}_{19/2}$), 350 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{M}_{15/2}, ^6\text{P}_{7/2}$), 357 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{I}_{11/2}$), 386 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{I}_{13/2}, ^4\text{F}_{7/2}$), 425 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{G}_{11/2}$), and 452 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$).²⁴ On the other hand, the excitation spectrum monitoring the Tm^{3+} emission at 455 nm,

 Fig. 2. (a, b) FESEM images of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},0.02\text{Dy}^{3+}$.

 Fig. 3. PL and PLE spectra of samples: (a) $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.02\text{Dy}^{3+}$ and (b) $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}$; the inset shows the dependence of the intensity on the Dy^{3+} (a) and Tm^{3+} (b) concentration.

in which the Dy^{3+} emission is very weak, reveals the same excitation band at 357 nm observed in Fig. 3b.

Comparing the Dy^{3+} and Tm^{3+} excitation band intensities, it can be observed that the excitations at

 Fig. 4. Excitation spectra of $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphor, monitoring the Tm^{3+} and Dy^{3+} emissions at 455 nm (solid line) and 580 nm (short-dashed line), respectively.

350 nm, 357 nm, and 363 nm could modulate the relative intensity of the Dy^{3+} and Tm^{3+} ion emissions.

To clarify this point, Fig. 5 shows the emission spectra of the $\text{Tm}^{3+}/\text{Dy}^{3+}$ -codoped $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphor under excitation at wavelength of 350 nm, at which Dy^{3+} ions are strongly excited, which can also appear in the blue and yellow emission spectra of Tm^{3+} ions (455 nm) and Dy^{3+} ions (580 nm). Moreover, weak emission peaks at 532 nm and 653 nm from Dy^{3+} can also be observed. However, the emission peak of Dy^{3+} ions is centered at 480 nm and covers the emission peak at 478 nm from the Tm^{3+} ions. In the emission spectrum of the codoped phase under excitation of 365 nm, although there are two rare-earth ion emission peaks, the blue and yellow light emission intensities are still lower than those in the emission spectra under excitation at wavelengths of 350 nm and 357 nm. According to these spectra, the emission intensity of the rare

Fig. 5. Emission spectra of the sample at λ_{ex} of 350 nm, 357 nm, and 365 nm.

Fig. 6. Emission spectra of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, x\text{Dy}^{3+}$ phosphors; insets show the intensities of Tm^{3+} and Dy^{3+} as functions of x and corresponding photographs under 357-nm UV lamp.

earth could be adjusted by changing the excitation wavelength, enabling fine-tuning of the luminescence color. Considering the synchronous emissions of the $\text{Tm}^{3+}/\text{Dy}^{3+}$ -codoped $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors, an appropriate excitation wavelength is 357 nm. The excitation bands of Dy^{3+} and Tm^{3+} overlap from 350 nm to 370 nm. This shows that both Tm^{3+} and Dy^{3+} singly doped $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors could be efficiently excited by UV light. Therefore, 357 nm was chosen as an appropriate excitation wavelength for these phosphors.

Figure 6 shows the emission spectra of the $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, x\text{Dy}^{3+}$ phosphors under excitation at 357 nm. The luminescence intensity increased as the doping concentration in the phases was increased from 0.01 mol to 0.025 mol. Comparison of the spectra in Fig. 3a indicates that the

Fig. 7. Decay times of samples at wavelengths of (a) 455 nm and (b) 580 nm.

content of Dy^{3+} had an important effect on the luminescence properties of the samples for given Tm^{3+} content. It is observed that the intensity of the blue emission (455 nm) due to the $^1\text{D}_2 \rightarrow ^3\text{F}_4$ transition of Tm^{3+} gradually decreased with increase of the Dy^{3+} concentration, demonstrating the occurrence of ET from Tm^{3+} to Dy^{3+} ions.

Evidently, the relative intensity of the blue emission (480 nm), yellow emission (580 nm), and red emission (653 nm) derived from the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_J$ ($J = 15/2, 13/2, 11/2$) transition of Dy^{3+} ions increased with increase of the Dy^{3+} ion concentration, clearly revealing energy transfer (ET) from Tm^{3+} to Dy^{3+} ions. The maximum intensity of the 580 nm emission was observed at 0.02 mol Dy^{3+} ion concentration. In other words, the relative intensity of the yellow versus blue emission changed with increase in the Dy^{3+} ion concentration.²⁴ In general, concentration quenching of Dy^{3+} activators is caused by ET from one activator (donor) to another until the energy sink (acceptor) in the lattice is reached. Hence, such ET strongly depends

 Fig. 8. Energy transfer process of Dy^{3+} and Tm^{3+} in the phosphors.

 Table I. CIE coordinates and CCT of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},x\text{Dy}^{3+}$ phosphors

Label	Sample	Excitation (nm)	CIE (x, y)	CCT (K)
1	$\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}$	357	(0.1855, 0.0942)	3734
2	$\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},0.01\text{Dy}^{3+}$	357	(0.2162, 0.2489)	41743
3	$\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},0.012\text{Dy}^{3+}$	357	(0.3195, 0.2553)	6700
4	$\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},0.015\text{Dy}^{3+}$	357	(0.3021, 0.3217)	7201
5	$\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},0.02\text{Dy}^{3+}$	357	(0.3371, 0.3431)	5295

on the average distance R_c between activators, which can be estimated using the equation^{26–28}

$$R_c \approx 2 \left(\frac{3V}{4\pi x_c N} \right)^{1/3}, \quad (1)$$

where V is the unit cell volume, x is the total concentration of the sensitizer and activator in the host, and N is the number of sites that the activator ion can occupy in the host. Under the present conditions, $N = 8$ and $x_c = 0.026$. Therefore, the critical distance $R_{\text{Tm-Dy}}$ can be calculated to be about 15.8 Å, much longer than 5 Å, the Tm–Dy distance at which it has been reported that ET becomes ineffective.²⁷ Therefore, we consider that concentration quenching should proceed via a phonon-assisted dipole or multipole ET mechanism.

Furthermore, to confirm ET between Tm^{3+} and Dy^{3+} ions, PL decay studies were performed on $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},x\text{Dy}^{3+}$ ($0 \leq x \leq 0.02$) phosphors. Figure 7a shows the luminescence decay ($^1\text{D}_2 \rightarrow ^3\text{F}_4$ transition) behavior of a series of

$\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},x\text{Dy}^{3+}$ phases under excitation at wavelength of 357 nm. The resulting decays can be fit using a single exponential. However, when the dopant ion concentration is large enough, ET appears and the decay curves become nonexponential. From all these decay curves, it is clearly observed that, with increase in the Dy^{3+} ion concentration, for all the codoped phosphors, the lifetime of the blue (455 nm) emission band of Tm^{3+} decreased, while that of the yellow (580 nm) emission band of Dy^{3+} increased (Fig. 6), in accordance with the recent report by Yu et al.^{25–28} The luminescence lifetime (τ) can be calculated using the following equation:

$$\tau = \int I(t)dt/I_0, \quad (2)$$

where $I(t)$ is the luminescence intensity as a function of time t , and I_0 is the maximum of $I(t)$, which occurs at the initial time t_0 .²⁸ The lifetime values calculated according to Eq. 2 under emission at 455 nm are depicted in Fig. 7a. It can be observed

that the lifetime values of the 455-nm emission decreased from 20.76 μs to 14.82 μs with increase in the Dy^{3+} ion concentration, clearly revealing that ET from Tm^{3+} to Dy^{3+} became much stronger as the Dy^{3+} ion concentration was increased, because of the close proximity of the Tm^{3+} and Dy^{3+} ions. The lifetime values of the 580-nm emission attributed to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transition of Dy^{3+} ions increased from 0.37 ms to 0.62 ms as the Dy^{3+} ion concentration was increased from 0 mol to 0.02 mol (Fig. 7b). Figures 7 and 8 show that these results are in good agreement with the results of the spectral measurements. From the values obtained in the decay lifetime studies, the Tm^{3+} -to- Dy^{3+} ET efficiency can be calculated using the following equation²⁸:

$$\eta_T = 1 - \tau_s/\tau_{s0}, \quad (3)$$

where τ_{s0} and τ_s are defined as the lifetimes for the Tm^{3+} -doped and $\text{Tm}^{3+}/\text{Dy}^{3+}$ -codoped sample, respectively. The efficiency of energy transfer (η_T) varied as a function of the Dy^{3+} concentration, increasing gradually to reach approximately 42.1% as the Dy^{3+} concentration reached its maximum value of 0.02 mol. It is pertinent to point out that the value obtained in the current study is very close to that reported for $15\text{SrO}-43\text{ZnO}-40\text{P}_2\text{O}_5-2\text{TiO}_2:0.8\text{-Dy}^{3+},0.6\text{Tm}^{3+}$ phosphor (showing record efficiency of about 33.41%).²⁹ Besides, according to the Dexter theory, if the ET mechanism between two activator ions occurs when monitoring with the dominant wavelength of the activator ions, the activator ion excitation spectrum should include a sensitizer ion excitation peak. This is also the basis for the energy transfer. Therefore, the ET mechanism between Tm^{3+} and Dy^{3+} ions corresponds to a resonance ET process.³⁰

The Commission Internationale de l'Éclairage (CIE) chromaticity coordinates calculated for $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},x\text{Dy}^{3+}$ at 357 nm are shown in Fig. 9 and presented in Table I. The coordinates (0.1855, 0.0942) for the Tm^{3+} -doped phase are indicated by point "a" in Fig. 9, corresponding to blue light. Moreover, it can be seen that the color tone changed from the edge of the white area to warm white with increase in the doping concentration of Dy^{3+} . For the $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},0.02\text{Dy}^{3+}$ codoped phase, the calculated coordinates were (0.3371, 0.3431), extremely close to those of standard white light (0.33, 0.33) with correlated color temperature (CCT) of 5295 K. Based on the intense white emission and improved coordinate values, it can be asserted that the current studied phosphor is a promising candidate for use in UV-converted white LEDs.

The thermal quenching properties of phosphors for application in solid-state lighting, particularly in high-power LEDs, deserve consideration, since they represent important technological parameters.³¹⁻³⁴ The temperature dependence of the PL spectrum in the temperature range from 293 K to 473 K was

Fig. 9. CIE coordinates of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},x\text{Dy}^{3+}$.

Fig. 10. Temperature dependence of emission spectra of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+},0.02\text{Dy}^{3+}$; inset shows a plot of $\ln[I_0/I(T) - 1]$ as a function of temperature.

therefore measured and is displayed in Fig. 10. The normalized integrated PL intensity varied as a function of temperature, as shown in the inset. The PL intensity decreased slightly while the intensity retention was 79.8% at temperatures as high as 473 K. Figure 10 demonstrates that the obtained compounds showed good thermal stability. To better elaborate the thermal quenching behavior of the compounds, their activation energies were also calculated based on the Mott equation,³⁵

$$I(T) \approx \frac{I_0}{1 + \exp\left(\frac{-\Delta E}{kT}\right)}, \quad (4)$$

where I_0 is the initial intensity, $I(T)$ is the intensity at temperature T , c is a constant, ΔE is the activation energy for thermal quenching, and k ($k = 8.629 \times 10^{-5}$ eV) is Boltzmann's constant.³⁶ The relationship between $\ln[(I_0/I_T) - 1]$ and $1/kT$ is linear with slope of -0.31 , as indicated in the inset of Fig. 10. For comparison, in analogous reports, the PL intensity of a $\text{NaGd}(\text{WO}_4)_2:\text{Tm}^{3+}$, Dy^{3+} , Eu^{3+} sample from the three emission centers (Tm^{3+} , Dy^{3+} , and Eu^{3+}) decreased to 73.9%, 57.5%, and 51.6%, respectively, at 473.15 K versus the initial value at 298.15 K.³⁷ A relatively high activation energy was obtained in the present work, suggesting that the phosphors showed good thermal stability and represent potential candidates for use in high-power LED applications.

CONCLUSIONS

A series of Tm^{3+} - and Dy^{3+} -doped and $\text{Tm}^{3+}/\text{Dy}^{3+}$ -codoped $\text{Ca}_2\text{Al}_2\text{SiO}_7$ phosphors were synthesized by high-temperature solid-state reaction. Effective ET from Tm^{3+} to Dy^{3+} was observed, reaching efficiency of around 42.1% at $x = 0.02$. At temperature of 473 K, the emission intensity of $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, 0.02\text{Dy}^{3+}$ decreased to 79.8% of the initial value at room temperature, and the activation energy ΔE was calculated to be 0.31 eV, confirming the good thermal stability of the $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, 0.02\text{Dy}^{3+}$ phosphor. Finally, the $\text{Ca}_2\text{Al}_2\text{SiO}_7:0.006\text{Tm}^{3+}, x\text{Dy}^{3+}$ phosphors exhibited great potential for use as single-component phosphors for ultraviolet white light-emitting diodes (UV w-LEDs).

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