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Remote Control Effect of Li^+ , Na^+ , K^+ Ions on the Photoluminescence Intensity of $\text{ZnTiO}_3:\text{Eu}^{3+}$ Nanomaterial

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ABSTRACT

Alkali metal ions (Li^+ , Na^+ & K^+) co-doped $\text{ZnTiO}_3:\text{Eu}^{3+}$ red emitting nano-phosphors series were prepared by combustion synthesis method. The crystal structure & surface morphology of the phosphors was analyzed by using X-ray diffraction (XRD) and Scanning electron microscopy (SEM) technique. The XRD results show the hexagonal phase of ZnTiO_3 with space group $R\text{-}3\text{:}R$. From the SEM results, it was observed that the phosphors had very small particle size ranging from 10-30nm and the average size of the ZnTiO_3 crystal is $30\pm 5\text{nm}$. Photoluminescence study showed that under the excitation of UV (393 nm) or blue light (464 nm), the obtained products emitted characteristic red emissions of Eu^{3+} at 615 nm for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition which proved that activator Eu^{3+} ion had successfully entered the host lattice of ZnTiO_3 . The red emission intensity was significantly enhanced by introducing alkali metal ions as co-dopants. A remarkable increase in the photoluminescence intensity is found by co-doping with Li^+ ions in $\text{ZnTiO}_3:\text{Eu}^{3+}$ lattices due to the reduction of environment symmetry around Eu^{3+} ions which strengthen the electric dipole transition.

Keywords: $\text{ZnTiO}_3:\text{Eu}^{3+}$, Alkali metal ions, Nano-phosphors Crystal, Photoluminescence.

1. INTRODUCTION

Luminescence is especially useful to probe the local structure of luminescent centers in a host lattice because of its simple energy level structure, great sensitivity to ligand field, and similar lanthanide chemical properties to the other rare earth ions [1-2]. Growing interest recently has focused on luminescence of trivalent rare earth ions in phosphates, tungstates, borates, molybdates, and aluminates, among which rare earth doped borates are especially attractive because of their wide UV transparency, exceptional optical damage thresholds, excellent chemical and thermal stability, and high luminescence efficiency [3-10]. The luminescence study of a series of such compounds provides much valuable information for optical applications [11-13]. However, the development of flat panel displays, such as field emission displays (FEDs), plasma display panels (PDPs) and thin film electro-luminescent devices (TFEL), and white light emitting diode (LED) have emerged as the principal motivation for research into rare-earth luminescence, therefore the present article concentrates on the variety of different ways in which rare-earth luminescence has been exploited in this field [14-17]. White light-emitting diodes (WLED) have attracted considerable attention because of their advantages of environment-friendly, high luminous efficiency, long lifetime and energy-saving [18-19]. One approach has been employed in mixing red, green and blue (RGB) phosphors in an appropriate proportion [20-22] for obtaining the best result. Therefore, it is urgent to find new red-emitting phosphors with excellent performance for WLED. Among the rare-earth ions, trivalent europium (Eu^{3+}) is an excellent activator for producing red light due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_x$ ($x = 0, 1, 2, 3, 4$) transitions [23-25]. As a potential inorganic compound, Zinc titanate (ZnTiO_3) have been mainly focused on its electrical, physical and photo-electrochemical properties, but not much on photoluminescence [26-27]. Wang *et al.* reported that ZnTiO_3 could be a promising host lattice for luminescent materials [28-29], and in recent years, researches have focused on improving its luminescence properties [30-31]. Chen *et al.* studied that when the localized surface plasmon resonance (LSPR) excitation spectrum of Ag nano-particles matched well with the excitation (430nm) emission (950 nm) wavelength, the PL intensity of $\text{CaTiO}_3:\text{Eu}^{3+}$ phosphor would be efficiently enhanced by about 1.8 times [32]. Wang *et al.* also reported that the normalized emission intensities of $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Eu}^{3+}$ could be distinctly enhanced by about 2.6 times by doping a series of M^+ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) into $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Eu}^{3+}$ [33]. Huang *et al.* studied the effect of alkali metal ions (Li^+ , Na^+ , K^+) on the local structure and luminescence for double tungstate compounds $\text{MEu}(\text{WO}_4)_2$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) prepared by a dual-space arches, indicating the alkali

metal ions could lead to some positive effects [34]. These ions enter into the host lattice and thus act as sensitizer or flux, bringing about oxygen vacancies or changing the crystal field surrounding the activator, and then influencing the photoluminescence performance [35-37]. Here we applied the combustion synthesis [38] for the preparation of europium doped Zn titanates phosphors which involved fast & thermal decomposition of the rare earth nitrate in the presence of an organic fuel like urea, hexamethylenetetramine as a combustion fuel. During high-temperature combustion reaction inside muffle furnace, many gases like CO₂, N₂, NO₂ etc as well as a large amount of heat are released within a short period of time thus resulting in a white, fluffy phosphor from metal nitrates ignited. This method has been utilized with the aim to prepare nano-sized crystalline powders of ZnTiO₃ doped with Eu³⁺ and co-doped with charge compensators like especially mono-valent cations after sintering at 1000 °C. Here the effect of addition of monovalent ions (Li⁺, Na⁺, K⁺) into ZnTiO₃ lattices to enhance the luminescence intensity had been studied and the possible mechanism has been proposed. In this work, we report a significant enhancement in red emission intensity of ZnTiO₃:Eu³⁺ nano-phosphor by introducing alkali metal ions as co-dopants. Hence the influences of addition of alkali metal ions on the energy transfer process and also on luminescence intensity is discussed in detail and the most suitable one has been determined.

2. EXPERIMENTAL

Synthesis & Characterization of ZnTiO₃:Eu³⁺,M⁺(M⁺=Li, Na, K) Nanophosphors:

Stoichiometric amounts of highly purity (99.9%) TiO₂ (1.0 mol), [(Zn(NO₃)₂), [Eu(NO₃)₃], [LiNO₃], [NaNO₃], [KNO₃] and Urea as a combustion fuel were used as a starting materials for the synthesis of Eu³⁺ doped ZnTiO₃ and M⁺ co-doped ZnTiO₃:Eu³⁺,M⁺ nano-crystals (M⁺= Li⁺, Na⁺, K⁺) with general formula Zn_(1-x)TiO₃:Eu_x³⁺ and Zn_(1-x+y)TiO₃:Eu_x³⁺, M_y⁺ where x is 0.5 to 3 mol % & y is 1 to 5mol %. A stoichiometric amount of metal nitrates and urea were calcined inside muffle furnace at 1000 °C for 3 h to obtain pure the crystalline form of the nano- phosphor.

The as-prepared solid solutions of different compositions were characterized by x-ray diffraction, scanning electron microscope, and photoluminescence techniques. Color purity was determined by chromaticity co-ordinates analysis. The measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Crystal Structure Analysis:

The crystal structure and phase purity were examined by X-ray diffraction patterns of ZnTiO₃ phosphors are shown in Fig. 1. It showed that all diffraction peaks of the samples were well matched with that of hexagonal-phase of ZnTiO₃ (JCPDS- No. 26-1500). It also indicates that the Eu³⁺ and M⁺ (M⁺= Li⁺, Na⁺, K⁺) ions were incorporated into the host lattice successfully and no secondary phase was found from the xrd pattern. The structure of hexagonal ZnTiO₃ can be further well described by space group R-3:R with lattice constants $a = b = 5.0787$, $c = 13.927$ Å. As shown in Fig. 2, it is observed that two Zn²⁺ ions may be replaced by one Eu³⁺ and one M⁺ ion so as to get charge balance, but the experimental results are more complicated.

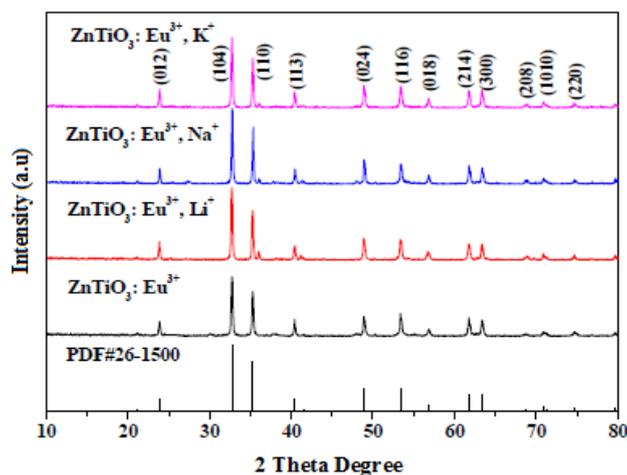


Fig. 1. XRD Pattern of ZnTiO₃:Eu³⁺ and M⁺ (M = Li, Na, K) Calcined at 1000 °C for 3 h.

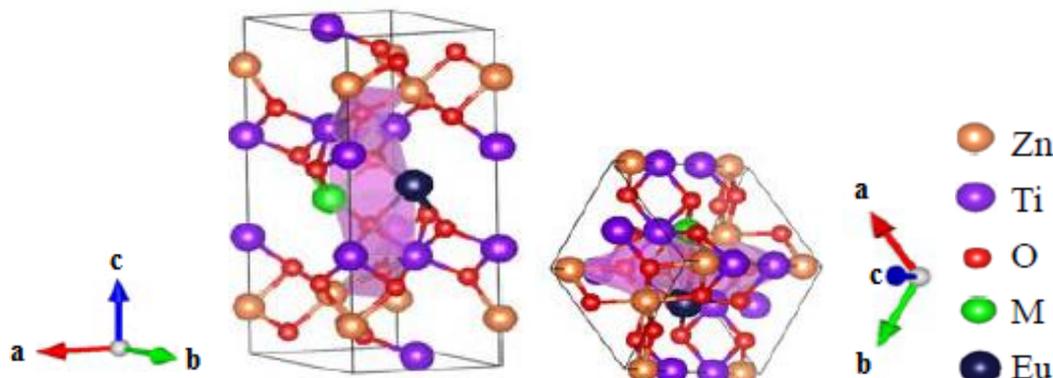


Fig. 2. Crystal Structure of Hexagonal ZnTiO₃ and Schematic Diagram of the Substitution by Eu³⁺/M

SEM Micrograph and Particle Size Analysis:

The photoluminescence is strongly affected by the crystallinity, particle size and surface roughness of the phosphor. Fig. 3 (a) & (b) shows the SEM images of the ZnTiO₃:Eu³⁺ and Li-doped ZnTiO₃:Eu³⁺ nano-particles which also support the hexagonal structures of ZnTiO₃:Eu³⁺ and Li⁺ co-doped ZnTiO₃:Eu³⁺. The particle shows good uniformity, smooth and dense microstructures with sizes range around 10~30 nm.

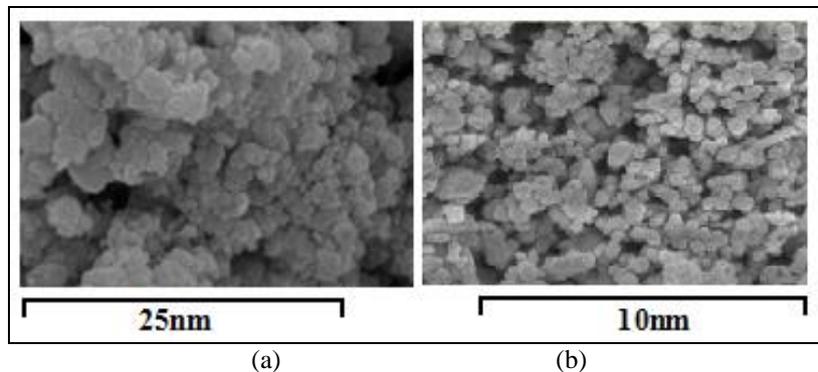


Fig. 3. SEM Images of (a): ZnTiO₃:Eu³⁺(2%) and (b): ZnTiO₃: Eu³⁺(2) ,(2%) Li⁺ Phosphors

Luminescence Properties Analysis:

Figs. 4 and 5 depict the excitation and emission spectra of ZnTiO₃:Eu³⁺ and M⁺ (M⁺ = Li⁺, Na⁺, K⁺) polycrystalline sample. It can be clearly seen that their regular patterns and peak positions of each curve are almost similar with variable intensity. The result indicates that the incorporation of alkali metal ions into ZnTiO₃:Eu³⁺ leads to a minor effect on the splitting of Eu³⁺ and energy level shift [39].

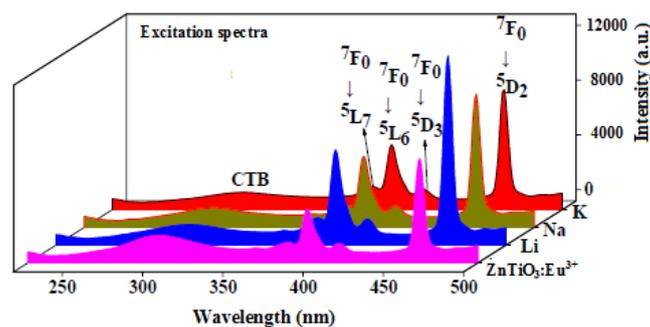


Fig. 4. Excitation Spectra of ZnTiO₃:2%Eu³⁺ & 2%M⁺=Li, Na, K (λ_{em}= 615nm)

Fig. 4 shows the excitation spectra of samples monitored at 615nm. The broad bands from 250 to 350 nm are mainly attributed to the charge transfer (CT) transition from O²⁻ to Eu³⁺ [40]. The excitation peak located at 464 nm is assigned to the ⁷F₀ → ⁵D₂ transition, and less intense absorption at 393, 385 and 414 nm is assigned to ⁷F₀ → ⁵L₆, ⁷F₀ → ⁵L₇ and ⁷F₀ → ⁵D₃, respectively [41]. As indicated in Fig. 5, the emission intensities of ZnTiO₃:Eu³⁺, M⁺ (M⁺ = Li⁺, Na⁺, K⁺) are found to be stronger than that of ZnTiO₃:Eu³⁺ phosphors. Thus, the relative's intensity of the emission spectrum of Li⁺, Na⁺ and K⁺ co-doped samples were increased by 1.63, 1.41 and 1.22 when compared to that of _{99.08}ZnTiO₃:_{0.02}Eu³⁺. It indicates that the incorporation of alkali metal ions (Li⁺, Na⁺, K⁺) can effectively enhance the luminescence intensity of the ZnTiO₃:Eu³⁺ phosphor. This phenomenon can be probably contributed to the fact that the effective ionic radius of Li⁺ ion (R_{Li⁺} = 59 pm, R_{Na⁺} = 99 pm & R_{K⁺} = 137 pm) is nearly the same as that of Zn²⁺ (R_{Zn²⁺} = 60 pm) and the Zn²⁺ can be easily replaced by Li⁺ [42].

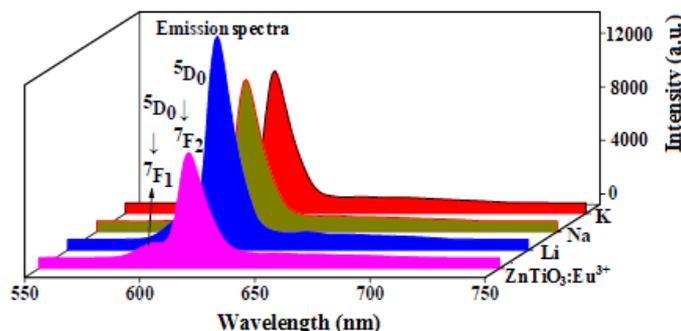


Fig. 5. Emission Spectra of ZnTiO₃:2%Eu³⁺ & 2%M⁺=Li, Na, K (λ_{ex} = 464nm)

Therefore, this substitution in the lattice induced faster energy transfer from the host to the Eu^{3+} ion, and hence created an increase in the hole concentration leading to a decrease in competitive absorption, as a result to a higher quantum yield [43]. According to Dexter's theory [44], the multipolar interaction occurring between the same activators can be calculated by the formula (1) given below:

$$\frac{1}{x} = K[1 + L(x)^{Q/3}]^{-1} \quad (1)$$

where K and L are constants for the given host, x is the activator concentration, and Q is the constant of multipolar interaction which equal to 10, 8, and 6 for quadrupole - quadrupole (q-q), dipole-quadrupole (d-q) and dipole-dipole (d-d) interactions, respectively. Fig. 6 shows the relation between $\log(I/x)$ and $\log(x)$ $\text{ZnTiO}_3:\text{Eu}^{3+}$ phosphor under the Eu^{3+} concentration of 1%, 1.5%, 2%, 2.5%. The slope of the curve is found to be -1.96 . The value of Q is calculated to be 5.89 which is close to 6, suggesting that dipole-dipole (d-d) interaction is the main mechanism for the concentration quenching [45] between Eu^{3+} ions and the $\text{ZnTiO}_3:\text{Eu}^{3+}$ phosphor. The emission intensities of $\text{ZnTiO}_3:\text{Eu}^{3+}, \text{M}^+$ phosphors are given in Fig. 7(a). The results show that the emission intensity increases with increasing the M^+ concentration at first, and then decreases when it reaches a maximum value of 4 mol%. When the content of alkali metal ions is less than 2 mol%, the emission intensity can be improved because Eu^{3+} can partially substitute Zn^{2+} , and then offset unbalanced charge between Eu^{3+} and Zn^{2+} [41]. When the content of alkali metal ions is more than 2 mol% and less than 4 mol%, the luminous intensity of samples is further improved. It is considered as the energy transfer enhanced between the substrate (ZnTiO_3) and activator (Eu^{3+}) with the alkali metal ions concentration increasing. However, when the content of alkali metal ions is higher than 4 mol%, the host lattice integrity was destroyed. As a consequence, ZnTiO_3 phosphor luminescence intensity decreased. Moreover, it is considered that the ions ($\text{Li}^+, \text{Na}^+, \text{K}^+$) substituting for Zn^{2+} could create point defects such as oxygen vacancies. The differences in charge number and radius values between alkali metal ions, Eu^{3+} and Zn^{2+} , will cause the formation of a bond electron-hole pair and change the Eu-O distance slightly [46]. The different alkali metal ions had a different effect on the relative intensities of $\text{ZnTiO}_3:\text{Eu}^{3+}$. Therefore, the relative intensities of excitation and emission for $\text{ZnTiO}_3:\text{Eu}^{3+}, \text{M}^+$ was found to be different.

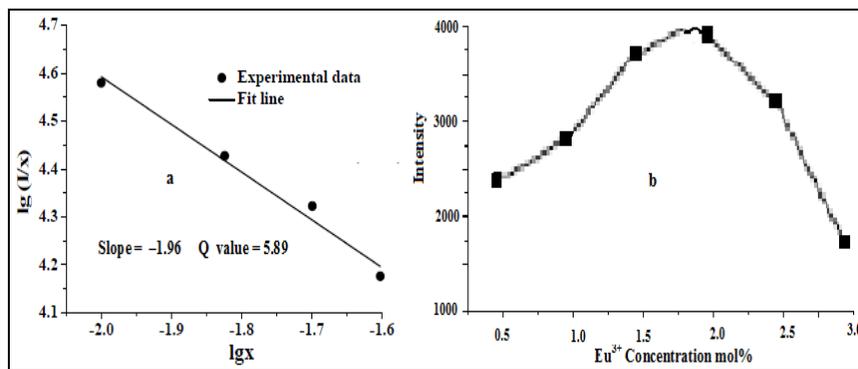


Fig. 6. (a) Plot of $\lg(I/x)$ as a Function of $\lg(x)$ and (b) Intensity v/s in Eu^{3+} mol% conc. in $\text{ZnTiO}_3:\text{Eu}^{3+}, \text{M}^+$ Phosphors ($\lambda_{\text{ex}}= 464\text{nm}$)

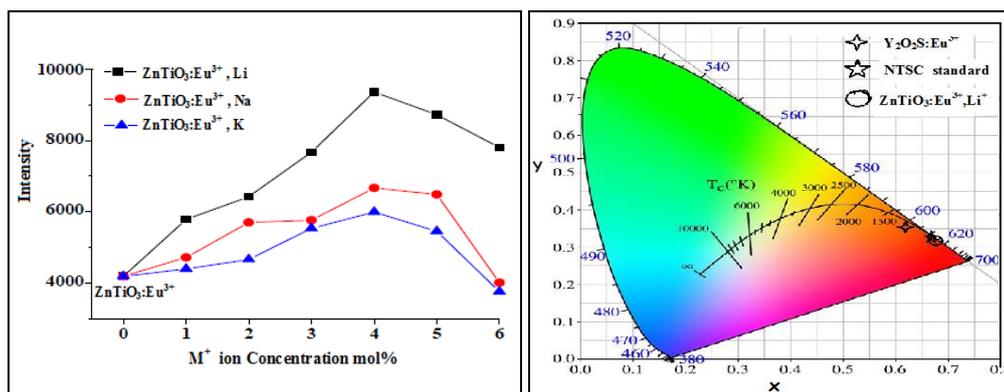


Fig. 7. (a) Normalized Intensities of $\text{ZnTiO}_3:\text{Eu}^{3+}, \text{M}^+$ [$\text{M}^+ = \text{Li}, \text{Na}, \text{K}$] conc. ($\lambda_{\text{ex}} = 464\text{nm}$) (b) CIE 1931 Chromaticity Coordinates of $\text{ZnTiO}_3:\text{Eu}^{3+}$ and $\text{ZnTiO}_3:\text{Eu}^{3+}, \text{M}^+$ ($\text{M} = \text{Li}$)

Chromaticity Co-ordinates Analysis:

CIE 1931 chromaticity coordinates of $\text{ZnTiO}_3:\text{Eu}^{3+}$ and $\text{ZnTiO}_3:2\%\text{Eu}^{3+}, 4\%\text{Li}^+$, and the national television standard committee (NTSC) standard for red and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ are shown in Fig. 7(b), which are calculated by the CIE 1931 color matching functions [47]. The calculated value for CIE coordinates for $\text{ZnTiO}_3:2\%\text{Eu}^{3+}, 4\%\text{Li}^+$ are found to be $x = 0.672$ and $y = 0.329$, similar to the standard red color (0.670, 0.330) in the NTSC system.

4. CONCLUSION

A series of $\text{ZnTiO}_3:\text{Eu}^{3+}, \text{M}^+$ ($\text{M}^+ = \text{Li}, \text{Na}, \text{K}$) red emitting nano-phosphors were successfully synthesized by combustion method. The XRD and SEM results show the ZnTiO_3 nano-particles exhibit a hexagonal phase with particle sizes range around 10 to 30

nm. When phosphors excited by blue light having wavelength 464nm, emitting intense-red photoluminescence peak at 615nm. The photoluminescence intensity is optimized by co-doping of some alkali metal ions having a concentration of 4 mol%. At 4 mol% the Li^+ , Na^+ and K^+ ions co-doped into $\text{ZnTiO}_3:2\%\text{Eu}^{3+}$, the normalized intensity of $\text{ZnTiO}_3:2\%\text{Eu}^{3+}$ is increased by 2.1, 1.7 and 1.4 times compared with $\text{ZnTiO}_3:2\%\text{Eu}^{3+}$. The CIE chromaticity coordinates of the $\text{ZnTiO}_3:2\%\text{Eu}^{3+}$, Li^+ phosphors are similar to the National Television Standard Committee (NTSC) standard CIE chromaticity coordinate values for red (0.670, 0.330). These results show that $\text{ZnTiO}_3:\text{Eu}^{3+}$, M^+ red-emitting phosphors can be applied in high-quality WLED potentially.

5. ACKNOWLEDGEMENT

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