Synthesis, photoluminescence and theoretical explanations of trivalent europium-doped dipotassium tungstate phosphors

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Abstract. Novel red-emitting europium-doped potassium tungstate phosphor has been successfully prepared through a solid-state reaction method. The phosphor exhibits sheet and polyporous morphology. The trivalent europium-doped potassium tungstate phosphor has the excellent red-emitting property due to the characteristic transitions of trivalent europium from 5D_0 to 7F_j . The critical concentration and critical distance are found to be about 2 mol% and 23.07 Å, respectively. The average CIE chromaticity coordinate of the europium-doped potassium tungstate phosphor upon 393 and 464 nm excitation is (0.64, 0.36), located in the red region. The luminescence decay time of the typical sample is 257 μs. Moreover, the photoluminescent excitation and emission spectra for europium ion at the potassium site of potassium tungstate crystal are well explained from a full energy matrix. All the results indicate that the europium-doped potassium tungstate phosphor is a potential red-emitting phosphor for near ultraviolet or blue light pumped light-emitting diodes.

Keywords: Photoluminescence, Phosphors, Solid state reaction, Crystal and ligand field, Potassium tungstate

1. Introduction

In recent years the solid-state lighting technology based on white light-emitting diodes (WLEDs), which are considered as energy-saving and environmentally friendly lighting sources, has attracted much attention in different application fields [1-6]. At present, the commercial WLEDs are made

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by integrating blue LED chips with yellow-emitting phosphors. However, this type of white light shows a low color rendering index ($R_a < 80$) due to deficiency of red color in emission. Thus, the most general approach to generate white light from LEDs is the combination of near-ultraviolet (n-UV) LEDs (emission at $\sim 370 - 400$ nm) or blue LEDs (~ 460 nm) with red, green, and blue phosphors [7-10]. In earlier works, the tungstate phosphors were investigated for luminescent applications [11-15]. Among them, potassium tungstate (K_2WO_4) was paid more attention because of its advantages such as low cost, good stability, and no toxicity [16, 17]. What's more, among rare-earth elements, trivalent europium (Eu^{3+}) is often used by researchers for making red-emitting phosphors where the prominent more than 600 nm emission band arises from electric dipole allowed transition [18-22]. However, as far as we know, there are no reports on rare-earth Eu^{3+} ions doped K_2WO_4 phosphors are available.

In this work, considering Eu^{3+} ions can readily occupy K^+ sites because ionic radius of K^+ (0.133 nm) is bigger than that of Eu^{3+} (0.095 nm) [23], we present the synthesis of $K_{2-x}WO_4: xEu^{3+}$ ($x=0, 0.5$ mol%, 1.0 mol%, 1.5 mol%, 2.0 mol%, 2.5 mol%, and 3.0 mol%) phosphors using a solid-state reaction method and investigate the photoluminescent characteristics. The structure, morphology, and photoluminescence properties are investigated in detail. The motivation of the study is not only to probe into the mechanisms of structural and luminescence properties but also to explore its potential application in LEDs. What's more, taking into account that a fundamental theoretical understanding of the photoluminescent excitation (PLEX) and emission (PLEM) mechanisms for Eu^{3+} ion at the K^+ site of K_2WO_4 crystal has not been set up, the explanation for energy levels of $K_2WO_4: Eu^{3+}$ by crystal-field theory is necessary. Thus, in this work, the fluorescent spectra for Eu^{3+} ion at the K^+ site of K_2WO_4 crystal are calculated by the full diagonalization (of energy matrix) method. The calculated data are compared with the experimental results.

2. Experimental Section

2.1 Preparation

Dipotassium tungstate with formula K_2WO_4 belongs to the family of perovskite compounds [16]. Until now, quite few phosphors' studies have been published on this compound in spite of the potential interest in many applications[17]. The conventional solid-state reaction is the most commonly used method for multicomponent phosphor powders synthesis with the advantage of its simplicity [24-27]. The starting materials used as received without further purification in the synthesis were K_2CO_3 (A.R.), WO_3 (A.R.), Eu_2O_3 (99.99%). The raw materials were finely ground. $K_2WO_4: Eu^{3+}$ has been produced by solid-state reaction process through sintering of K_2CO_3 , WO_3 , and Eu_2O_3 at temperature 400 °C for 2h and at 800 °C for 3h according to

The products were then cooled down to room temperature in the furnace, ground, and dried for further measurements.

2.2 Characterization

The phase purity of the samples was analyzed by X-ray diffraction (XRD) using a XRD-7000 type X-ray diffractometer with a $Cu\ K\alpha$ radiation ($\lambda=0.154056\text{ nm}$), operating at 30 kV and 15 mA. The morphology of the typical sample was examined using scanning electron microscopy (SEM; JEOL JSM-6380LA). The PLEM and PLEX spectra were recorded at room temperature using a Hitachi F-4600 fluorescence spectrophotometer equipped with a 150 W xenon light source. The PL decay curve was recorded using an FLS-980 fluorescence spectrophotometer (Edinburgh Instruments) equipped with both continuous and pulsed xenon lamps as the light source.

3. Results and Discussion

3.1 Crystal Structure

The crystallite size and surface morphology have strong effects on the photoluminescence properties of the phosphor materials. Fig. 1 (a) shows the XRD patterns of the phosphors with different doped doses. This crystal is a monoclinic structure with space group of $C_{2/m}$ and lattice parameters of $a=1.239(1)$ nm, $b=0.6105(5)$ nm, $c=0.7560(5)$ nm, $\beta=115.96(3)^\circ$, $Z=4$, and $V=0.51415$ nm³ [16]. The radii of Eu^{3+} (0.095 nm) are smaller than that of K^+ (0.133 nm) but bigger than that of W^{6+} (0.062 nm) [23]. Thus, the substitution of Eu^{3+} for K^+ ion at $4i$ site in the host structure is reasonable and desirable. Fig. 1 (a) shows the XRD pattern of $\text{K}_{2-x}\text{WO}_4: x\text{Eu}^{3+}$ compared with the standard data of K_2WO_4 (PDF#24-0905) [16]. It is obvious that all the diffractive peaks match well with the standard JCPDS card (PDF#24-0905). Hence, the results clearly suggest that Eu^{3+} ions enter into the matrix without changing the crystalline structure of the sample. The crystal structure of K_2WO_4 is displayed in Fig. 1 (b). From Fig. 1 (b), there is a tetrahedral and two octahedral structures including WO_4 , K_IO_6 and K_{II}O_6 to form a highly condensed network.

3.2 Morphology of the $\text{K}_2\text{WO}_4: \text{Eu}^{3+}$ Phosphor

Fig. 2 shows the typical SEM image of the $\text{K}_{1.98}\text{WO}_4: 0.02\text{Eu}^{3+}$ sample. The phosphors exhibit sheet and polyporous shape morphology with the length of particle size ranging from 1 to 3 μm .

3.3 Photoluminescence Properties

Fig. 3 illustrates the photoluminescence spectra of $\text{K}_{2-x}\text{WO}_4: x\text{Eu}^{3+}$ with varying Eu^{3+} concentrations. The excitation spectrum in Figure 3 (a) exhibits a broad band between 200 and 230 nm, which is ascribed to charge transitions (CT) from the oxygen 2p orbital to the tungsten's empty 5d orbital or to an europium's empty 4f orbital [28-30]. In the 310-490 nm spectral range, sharp peaks are ultraviolet and visible due to $4f \rightarrow 4f$ transitions which are assigned to $^7\text{F}_0 \rightarrow ^5\text{L}_J$ ($J=\text{D, H, L}$) of Eu^{3+} ion. The dominated peak is assigned to the ground

state 7F_0 to the excited state 5L_6 transition (electric dipole) at 393 nm. These narrow lines are assigned to transition from 7F_0 to ${}^5L_{6,7}$ (375, 379 and 393 nm), 5H_J (318 and 326 nm) and 5D_J (361, 364, 413, 464 and 471 nm) levels.

Fig. 3 (b) and (c) depict the emission spectrum of the non-doped and doped K_2WO_4 samples monitored under $\lambda_{ex}=393$ nm and blue light 464 nm, respectively. The ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ are typical magnetic and electronic dipole transitions, respectively, and they depend on the local symmetry of the Eu^{3+} ions. Due to the magnetic dipole-dipole transition, the ${}^5D_0 \rightarrow {}^7F_1$ transition cannot be expected to depend strongly on coordination [31, 32]. Thus, in this case, the ${}^5D_0 \rightarrow {}^7F_2$ electric dipole transition is dominant when Eu^{3+} occupies a non-centrosymmetric environment such as in the monoclinic framework. Emission spectra of all samples revealed transitions from 5D_0 excited levels to ground states 7F_J ($J = 0, 1, 2, 3$ and 4) of the Eu^{3+} at 584, 592, 615, 620, 657 and 706 nm, respectively. The ${}^5D_0 \rightarrow {}^7F_0$ transition shows only one band and hence the levels with $J=0$ are nondegenerate which indicates that the Eu^{3+} is located in $4i$ (K^+) sites having only one kind of symmetry [33-35]. From Fig. 3, the optimal/critical doping concentration was observed at $x=0.02$ mol; the concentration quenching was observed when the content of Eu^{3+} exceeds 0.02 mol. The concentration quenching is due to the nonradiative energy transfer between Eu^{3+} ions, the possibility of which increases as the concentration of Eu^{3+} increases. Here, we use the concentration quenching method to calculate the critical distance (R_c) [20, 36, 37]. The value of R_c can be calculated by the critical concentration of the activator ion,

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

where x_c is the critical concentration, Z is the number of formula units per unit cell, and V is the volume of the unit cell. For the K_2WO_4 host, when $Z = 4$, $x_c = 0.02$, and $V = 514.15 \text{ \AA}^3$, the obtained R_c value is $23.07 \text{ \AA}$, which is similar order of magnitude to the R_c value for Eu^{3+} centers in several oxide lattices [20, 38]. It is worth noting that this value is much farther than the distance of the nearest neighbor K^+ ions (no more than $5.5 \text{ \AA}$) according to the crystal structure results [16]. Thus, it is reasonable that the

concentration quenching of Eu^{3+} - Eu^{3+} ions in K_2WO_4 occurs at such a relatively low Eu^{3+} concentration.

The Eu^{3+} ion is expected to replace the K^+ ion it would be difficult to keep a charge balance in K_2WO_4 : Eu^{3+} phosphor. When a trivalent metallic ion such as Eu^{3+} is incorporated into a host lattice and substitutes for a monovalent metallic ion, charge balancing is necessarily required. Thus, in disordered dipotassium tungstate powders, oxygen vacancies can occur and capture electrons and then are neutral in relation to the lattice.

The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of the $\text{K}_{2-x}\text{WO}_4$: $x\text{Eu}^{3+}$ phosphors with different Eu^{3+} concentrations are summarized in Table 1. The emission bright red in the $\text{K}_{2-x}\text{WO}_4$: $x\text{Eu}^{3+}$ phosphors is clearly observed. The average chromaticity index is (0.64, 0.36) which is in the ideal red region. The chromaticity coordinate is excellent for a red phosphor and indicates that they are comparable to commercially available red phosphor used for n-UV or blue chip such as $\text{Y}_2\text{O}_2\text{S}$: Eu^{3+} (where $x'=0.64$, $y'=0.34$) [39].

3.4 Lifetime

Fig. 4 shows the decay curves of the $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition in typical $\text{K}_{1.98}\text{WO}_4$: 0.02Eu^{3+} sample, where excitation and emission wavelengths are fixed at 393 and 615 nm, respectively. The decay curves of Eu^{3+} is well fitted with a double exponential equation [40, 41],

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (3)$$

where I is the luminescence signal, A_1 and A_2 are constants, t is the time, τ_1 and τ_2 are lifetimes for exponential components. The double exponential nature is because of occupancies of two K^+ at $4i$ sites by Eu^{3+} ions in the host matrix, which is consistent with the XRD's result (see Fig. 1 (b)). The average decay time $\langle \tau \rangle$ can be determined by the formula,

$$\langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (4)$$

According to the above equation, the lifetime of Eu^{3+} ion in $\text{K}_{1.98}\text{WO}_4: 0.02\text{Eu}^{3+}$ can be obtained as 257 μs .

3.5 Crystal-Field Calculations

In order to simplify the calculation, many studies suggest higher site symmetry to remove the imaginary crystal-field parameters [42, 43]. Moreover, the high resolution hyperfine study is not involved in the present investigation. Thus, although it is actually a low symmetry $C_{2/m}$, a reasonable approximate D_{2h} site symmetry is proposed for rare-earth ion Eu^{3+} doped at the K^+ site. The effective operator Hamiltonian for rare-earth ions in crystals with D_{2h} site symmetry can be expressed as [44-48]

$$H = H_{\text{free ion}} + H_{CF}(D_{2h}) \quad (5)$$

in which the free ion Hamiltonian can be written as [46-49]

$$H_{\text{free ion}} = E_n + \sum_{k=2,4,6} \frac{F_k}{v} f \xi_k + A \alpha \left(L \cdot S \right) + \beta \left(G \right) G + \sum_{i=2,3,4,6,7} t_i T_i + \sum_{k=8} m_k M_k + \sum_{0,2k \neq 4} p^k P^k \quad (6)$$

The physical meanings of these free ion parameters have reported by Crosswhite and Carnall et al [47,48]. The crystal field Hamiltonian with D_{2h} site symmetry in the Wybourne notation can be given as [49, 50]

$$H_{CF}(D_{2h}) = B_{20}C_{20} + B_{20}(C_{2,-2} + C_{2,2}) + B_{40}C_{40} + B_{42}(C_{4,-2} + C_{4,2}) + B_{44}(C_{4,-4} + C_{4,4}) + B_{60}C_{60} + B_{62}(C_{6,-2} + C_{6,2}) + B_{64}(C_{6,-4} + C_{6,4}) + B_{66}(C_{6,-6} + C_{6,6}) \quad (7)$$

in which B_{kq} are the crystal-field parameters, and C_{kq} are the Racah spheric tensor operators. A full energy matrix is constructed from the effective operator Hamiltonian and then the energy-level of Eu^{3+} ion in K_2WO_4 crystal are calculated from this matrix. In the calculations, the free-ion parameters in the energy matrix remain fixed and taken as follows, $E_{av} \approx 64736.66 \text{ cm}^{-1}$, the Coulomb repulsions $F_2 \approx 84375 \text{ cm}^{-1}$, $F_4 \approx 60330.6 \text{ cm}^{-1}$, $F_6 \approx 41593.27 \text{ cm}^{-1}$, the spin-orbit coupling parameter $\zeta_{4f} \approx 1331 \text{ cm}^{-1}$, the two-body and three-body interaction parameters $\alpha \approx 16.8 \text{ cm}^{-1}$, $\beta \approx -640 \text{ cm}^{-1}$, $\gamma \approx 1750 \text{ m}^{-1}$, $T_2 \approx 370 \text{ cm}^{-1}$, $T_3 \approx 40 \text{ cm}^{-1}$, $T_4 \approx 40 \text{ cm}^{-1}$, $T_6 \approx -330 \text{ cm}^{-1}$, $T_7 \approx 380 \text{ cm}^{-1}$,

$T_8 \approx 370 \text{ cm}^{-1}$, the Marvin integrals $M_0 \approx 2.38 \text{ cm}^{-1}$, $M_2 \approx 1.33 \text{ cm}^{-1}$, $M_4 \approx 0.90 \text{ cm}^{-1}$, the parameters related to the electrostatic correlated magnetic interaction $P_2 \approx 245 \text{ cm}^{-1}$, $P_4 \approx 183.75 \text{ cm}^{-1}$, $P_6 \approx 122.5 \text{ cm}^{-1}$. The above parameters are similar or close to those of literature's report [51]. Thus, in the above full energy matrix, only the crystal-field parameters are unknown. These parameters are often taken as adjustable data because they depend upon the central rare-earth ion, the ligands and the nature of metal-ligand bonds. By fitting the calculated optical spectra to the observed values of the Eu^{3+} center in K_2WO_4 crystal, we get

$$\begin{aligned} B_{20} &\approx 407.95 \text{ cm}^{-1}, B_{22} \approx 887.68 \text{ cm}^{-1}, B_{40} \approx -500.59 \text{ cm}^{-1}, \\ B_{42} &\approx 1830.7 \text{ cm}^{-1}, B_{44} \approx -2051.37 \text{ cm}^{-1}, B_{60} \approx -384.06 \text{ cm}^{-1}, \\ B_{62} &\approx -441.5 \text{ cm}^{-1}, B_{64} \approx -1936.83 \text{ cm}^{-1}, B_{66} \approx 556.76 \text{ cm}^{-1} \end{aligned} \quad (9)$$

The comparisons between the calculated optical spectral data and the experimental values are listed in Table 2. Note that only some low-lying multiplets are given in Table 2. In addition, it should be pointed out that the local structural distortions caused by substituting Eu^{3+} for K^+ and the imaginary parts are not considered in crystal-field parameters, and these should cause a minor shift in optical band positions for $\text{K}_2\text{WO}_4: \text{Eu}^{3+}$ phosphor, and then there are some small errors between the calculated and experimental results (see Table 2).

4. Conclusions

A series of $\text{K}_{2-x}\text{WO}_4: x\text{Eu}^{3+}$ ($0 \leq x \leq 0.03$) phosphors were successfully synthesized through a facile and efficient solid-state method. XRD shows that the structure of the synthesized $\text{K}_2\text{WO}_4: \text{Eu}^{3+}$ monoclinic type is formed at 400°C for 2 h and 800°C for 3 h. The samples exhibit sheet and polyporous shape morphology. The $\text{K}_2\text{WO}_4: \text{Eu}^{3+}$ can be efficiently excited in the n-UV or blue chips. The CIE chromaticity coordinates of the $\text{K}_{2-x}\text{WO}_4: x\text{Eu}^{3+}$ phosphors are in the ideal red region. The quenching mechanism and charge balance in $\text{K}_2\text{WO}_4: \text{Eu}^{3+}$ phosphors are discussed. All the results indicate that the $\text{K}_2\text{WO}_4: \text{Eu}^{3+}$ phosphors have potential applications in both n-UV and blue LED which can be excited at around 393 and 464 nm. What's more, the calculated optical spectral data agree well with the experimental values (see Table

2) by using those suitable crystal-field parameters. The errors in Table 2 between calculated and experimented spectral values are so tiny, which suggests that the optical spectra of $\text{K}_2\text{WO}_4\text{:Eu}^{3+}$ phosphors can be explained reasonably by the diagonalization (of energy matrix) method for Eu^{3+} ion at approximate D_{2h} symmetry. Besides, the good agreement between theory and experiment has also testified that the Eu^{3+} replacing K^+ site in K_2WO_4 crystal is reasonable and this is also consistent with the present experimental results.

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References

- [1] Q. Zhang, C.F. Wang, L.T. Ling, S. Chen, Fluorescent nanomaterial-derived white light-emitting diodes: what's going on, *J. Mater. Chem. C* 2 (2014) 4358-4373.
- [2] Y.C. Chen, C.B. Siao, H.S. Chen, K.W. Wang, S.R. Chung, The application of $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$ nanocrystals in white light emitting diodes devices, *RSC Adv.* 5 (2015) 87667-87671.
- [3] C.C. Shen, W.T. Chen, R.S. Liu, Zeolitic imidazolate framework $[\text{Zn}_2(\text{IM})_4(\text{DMF})]$ for UV-white light-emitting diodes, *Dalton Trans.* 41 (2012) 11885-11888.
- [4] J.J. Huang, Y.B. Ye, Z.Q. Lei, X.J. Ye, M.Z. Rong, M.Q. Zhang, Highly luminescent and transparent ZnO quantum dots–epoxy composite used for white

- light emitting diodes, *Phys. Chem. Chem. Phys.* 16 (2014) 5480-5484.
- [5] H.J. Song, D.K. Yim, H.S. Roh, I.S. Cho, S.J. Kim, Y.H. Jin, H.W. Shim, D.W. Kim, K.S. Hong, $\text{RbBaPO}_4: \text{Eu}^{2+}$: a new alternative blue-emitting phosphor for UV-based white light-emitting diodes, *J. Mater. Chem. C* 1 (2013) 500-505.
- [6] G. Zhu, S. Xin, Y. Wen, Q. Wang, M. Que, Y. Wang, Warm white light generation from a single phased phosphor $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2): \text{Eu}^{2+}, \text{Mn}^{2+}, \text{Tb}^{3+}$ for light emitting diodes, *RSC Adv.* 3 (2013) 9311-9318.
- [7] C.H. Huang, T.M. Chen, Novel yellow-emitting $\text{Sr}_8\text{MgLn}(\text{PO}_4)_7: \text{Eu}^{2+}$ (Ln=Y, La) phosphors for applications in white LEDs with excellent color rendering index, *Inorg. Chem.* 50 (2011) 5725-5730.
- [8] Z. Xia, R.S. Liu, Tunable blue-green color emission and energy transfer of $\text{Ca}_2\text{Al}_3\text{O}_6\text{F}: \text{Ce}^{3+}, \text{Tb}^{3+}$ phosphors for near-UV white LEDs, *J. Phys. Chem. C* 116 (2012) 15604-15609.
- [9] J.K. Sheu, S.J. Chang, C.H. Kuo, Y.K. Su, L.W. Wu, Y.C. Lin, W.C. Lai, J.M. Tsai, G.C. Chi, R.K. Wu, White-light emission from near UV InGaN-GaN LED chip precoated with blue/green/red phosphors, *IEEE-Photon. Tech. Lett.* 15 (2003) 18-20.
- [10] C.C. Yang, C.M. Lin, Y.J. Chen, Y.T. Wu, S.R. Chuang, R.S. Liu, S.F. Hu, Highly stable three-band white light from an InGaN-based blue light-emitting diode chip precoated with (oxy) nitride green/red phosphors, *Appl. Phys. Lett.* 90 (2007) 123503.
- [11] G. H. Lee, T.H. Kim, C. Yoon, S. Kang, Effect of local environment and Sm^{3+} -codoping on the luminescence properties in the Eu^{3+} -doped potassium tungstate phosphor for white LEDs, *J. Lumin.* 128 (2008) 1922-1926.
- [12] W.L. Feng, C.Y. Tao, K. Wang, Synthesis and photoluminescence of tetravalent cerium-doped alkaline-earth-metal tungstate phosphors by a co-precipitation method, *Spectros. Lett.* 48 (2014) 381-385.
- [13] K. Wang, W.L. Feng, X. Feng, Y. Li, P. Mi, S.S. Shi, Synthesis and photoluminescence of novel red-emitting $\text{ZnWO}_4: \text{Pr}^{3+}, \text{Li}^+$ phosphors, *Spectrochim. A.* 154 (2016) 72-75.

- [14] G. Born, A. Hofstaetter, A. Scharmann, G. Schwarz, Luminescence mechanism of tungstate phosphors, *J. Lumin.* 1-2 (1970) 641-650.
- [15] Y.R. Do, Y.D. Huh, Optical properties of potassium europium tungstate phosphors, *J. Electrochem. Soc.* 147 (2000) 4385-4388.
- [16] A.S. Koster, F.X.N.M. Kools, G.D. Rieck, The crystal structure of potassium tungstate, K_2WO_4 , *Acta Cryst. B* 25 (1969) 1704-1708.
- [17] Y.A. Koksharov, A.V. Avdei, V.D. Dolzhenko, Y.M. Kiselev, EPR spectra of caesium and potassium molybdates and tungstates, *Mendeleev Commun.* 15 (2005) 77-79.
- [18] W.L. Feng, Y. Jin, Y. Wu, D.F. Li, A.K. Cai, Co-precipitation synthesis and photoluminescence properties of $Ba_{1-x}MoO_4:xEu^{3+}$ red phosphors, *J. Lumin.* 134 (2013) 614-617.
- [19] W.L. Feng, M.F. Zhao, J.Y. Xue, X.J. Tian, Photoluminescence properties of $(Ba_{1-x}Eu_x)WO_4$ red synthesized by the coprecipitation/calcination method, *J. Alloys Compd.* 521 (2012) 146-149.
- [20] H. Zhou, Q. Wang, Y. Jin, Temperature dependence of energy transfer in tunable white light-emitting phosphor $BaY_2Si_3O_{10}:Bi^{3+}, Eu^{3+}$ for near UV LEDs, *J. Mater. Chem. C* 3 (2015) 11151-11162.
- [21] G.S.R. Raju, E. Pavitra, G. Nagaraju, J.S. Yu, Versatile properties of $CaGd_2ZnO_5:Eu^{3+}$ nanophosphor: its compatibility for lighting and optical display applications, *Dalton Trans.* 44 (2015) 1790-1799.
- [22] B.P. Singh, J. Singh, R.A. Singh, Luminescence properties of Eu^{3+} -activated $SrWO_4$ nanophosphors-concentration and annealing effect, *RSC Adv.* 4 (2014) 32605-32621.
- [23] R.C. Weast, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 1989, F-187.
- [24] X. Feng, W. Feng, K. Wang, Experimental and theoretical spectroscopic study of praseodymium (III) doped strontium aluminate phosphors, *J. Alloys Compd.* 628 (2015) 343-346.
- [25] P. Kumari, J. Manam, Enhanced red emission on co-doping of divalent ions

- ($M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}$) in $YVO_4: Eu^{3+}$ phosphor and spectroscopic analysis for its application in display devices, *Spectrochim. A. A* 152 (2016) 109-118.
- [26] J.H. Lee, Y.J. Kim, Photoluminescent properties of $Sr_2 SiO_4: Eu^{2+}$ phosphors prepared by solid-state reaction method, *Mater. Sci. Eng. B* 146 (2008) 99-102.
- [27] K. Wang, X. Feng, W. Feng, S. Shi, Y. Li, C. Zhang, On the estimation of average crystallite size of zeolites from the Scherrer equation: a critical evaluation of its application to zeolites with one-dimensional pore systems, *Z. Naturforsch. A* 71 (2016) 21-25.
- [28] X. Feng, W. Feng, M. Xia, K. Wang, H. Liu, D. Deng, X. Qin, W. Yao, W. Zhu, Effect of surfactants on morphology and luminescent properties of $CaMoO_4: Eu^{3+}$ red phosphors, *RSC Adv.* 6 (2016) 14826-14831.
- [29] B.G. Wybourne, *Spectroscopic properties of rare earths*, New York: Wiley; 1965.
- [30] G.K. Liu, B. Jacquier, *Spectroscopic properties of rare earths in optical materials*, Springer; 2005.
- [31] S.J. Park, C.H. Park, B.Y. Yu, H.S. Bae, C.H. Kim, C.H. Pyun, Structure and luminescence of $SrY_2 O_4: Eu$, *J. Electrochem. Soc.* 146 (1999) 3903-3906.
- [32] K. Binnemans, Interpretation of europium (III) spectra, *Coordin. Chem. Rev.* 295 (2015) 1-45.
- [33] W.D. Horrocks, D.R. Sudnick, Lanthanide ion luminescence probes of the structure of biological macromolecules, *Acc. Chem. Res.* 14 (1981) 384-392.
- [34] D.K. Kölmel, B. Rudat, U. Schepers, S. Bräse, Peptoid-based rare-earth (Group 3 and lanthanide) transporters, *Eur. J. Org. Chem.* 2013 (2013) 2761–2765.
- [35] W.D. Horrocks Jr., D.R. Sudnick, Lanthanide ion probes of structure in biology. laser-induced luminescence decay constants provide a direct measure of the number of metal-coordinated water molecules, *J. Am. Chem. Soc.* 101(1979) 334-340.
- [36] G. Blasse, Energy transfer in oxidic phosphors, *Phys. Lett. A* 28 (1968) 444-445.
- [37] W.R. Liu, C.H. Huang, C.P. Wu, Y.C. Chiu, Y.T. Yeh, T.M. Chen, High efficiency and high color purity blue-emitting $NaSrBO_3: Ce^{3+}$ phosphor for near-UV light-emitting diodes, *J. Mater. Chem.* 21 (2011) 6869-6874.

- [38] H. Zhou, Y. Jin, M. Jiang, Q. Wang, X. Jiang, A single-phased tunable emission phosphor $\text{MgY}_2\text{Si}_3\text{O}_{10}:\text{Eu}^{3+}, \text{Bi}^{3+}$ with efficient energy transfer for white LEDs, *Dalton Trans.* 44 (2015) 1102-1109.
- [39] C.A. Kodaira, H.F. Brito, M.C.F.C. Felinto, Luminescence investigation of Eu^{3+} ion in the $\text{RE}_2(\text{WO}_4)_3$ matrix (RE= La and Gd) produced using the Pechini method, *J. Solid State Chem.* 171 (2003) 401-407.
- [40] Z. Xia, W. Wu, Preparation and luminescence properties of Ce^{3+} and $\text{Ce}^{3+}/\text{Tb}^{3+}$ -activated $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$ phosphors, *Dalton Trans.* 42 (2013) 12989-12997.
- [41] Y. Jin, J. Zhang, S. Lü, H. Zhao, X. Zhang, X. Wang, Fabrication of Eu^{3+} and Sm^{3+} codoped micro/nanosized MMoO_4 (M=Ca, Ba, and Sr) via facile hydrothermal method and their photoluminescence properties through energy transfer, *J. Phys. Chem. C* 112 (2008) 5860-5864.
- [42] C. Delsart, N. Pelletier-Allard, R. Pelletier, Zeeman effect of the 6011 Å line of $\text{Pr}^{3+}:\text{LaCl}_3$ using the fluorescence line-narrowing technique, *Opt. Commun.* 16 (1976) 114-117.
- [43] Y.Y. Yeung, P. A. Tanner, New analyses of energy level datasets for $\text{LaCl}_3:\text{Ln}^{3+}$ (Ln= Pr, Nd, Er), *J. Alloys Compd.* 575 (2013) 54-60.
- [44] M.F. Reid, L. van Pieterse, R.T. Wegh, A. Meijerink, Spectroscopy and calculations for $4f^N \rightarrow 4f^N \rightarrow 15d$ transitions of lanthanide ions in LiYF_4 , *Phys. Rev. B* 62 (2000) 14744-14749.
- [45] G.K. Liu, Systematics of f-element crystal-field interaction, *J. Solid State Chem.* 178 (2005) 489-498.
- [46] M. Karbowiak, C. Rudowicz, P. Gnutek, Energy levels and crystal-field parameters for Pr^{3+} and Nd^{3+} ions in rare earth (RE) tellurium oxides $\text{RE}_2\text{Te}_4\text{O}_{11}$ revisited—Ascent/descent in symmetry method applied for triclinic site symmetry, *Opt. Mater.* 33 (2011) 1147-1161.
- [47] H.M. Crosswhite, H. Crosswhite, Parametric model for *f*-shell configurations. I. The effective-operator Hamiltonian, *J. Opt. Soc. Am. B* 1 (1984) 246-254.
- [48] W.T. Carnall, G.L. Goodman, K. Ramjnak, R. S. Rana, A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3 , *J. Chem. Phys.* 90

(1989) 3443-3457.

- [49] K.A. Gschneidner, J.L. Eyring, Handbook of the physics and chemistry of rare earths, Vol. 23. Amsterdam: Elsevier, 1996.
- [50] B.G. Wybourne, Spectroscopic properties of rare earths. New York: Wiley, 1965.
- [51] W.Q. Yang, H.G. Liu, G.K. Liu, Y. Lin, M. Gao, X.Y. Zhao, W.C. Zheng, Y. Chen, J. Xu, L. Z. Li, Trivalent europium-doped strontium molybdate red phosphors in white light-emitting diodes: Synthesis, photophysical properties and theoretical calculations, *Acta Mater.* 60 (2012) 5399-5407.

Figures and Captions.

Fig. 1 (a) X-ray diffraction patterns and crystal structure of the europium-doped potassium tungstate phosphors. All main peaks can be indexed by a monoclinic structure with space group of $C_{2/m}$, indicating that the phase here is europium-doped potassium tungstate phosphors. (b) Crystal structure of potassium tungstate phosphor and coordination environment for potassium sites.

Fig. 2 Scanning electron microscopy image of 0.02 molar europium-doped potassium tungstate phosphor.

Fig. 3 Photoluminescence spectra of non-doped potassium tungstate and europium-doped potassium tungstate samples: (a) the emission at $\lambda_{\text{em}}=615\text{ nm}$; (b) the excitation at $\lambda_{\text{ex}}=393\text{ nm}$, and (c) $\lambda_{\text{ex}}=464\text{ nm}$.

Fig. 4 Selected decay curve of europium-doped potassium tungstate phosphor ($\lambda_{\text{ex}}=393$ nm, and $\lambda_{\text{em}} = 615$ nm)

Tables.

Table 1. Europium concentrations, normalized photoluminescence (PL) signal of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition and the Commission Internationale de l'Eclairage chromaticity (CIE) coordinates for europium-doped potassium tungstate phosphors

Eu ³⁺ concentration	Normalized PL signal (%)	CIE (x' , y')
$x=0.005$	22.3	(0.61,0.38)
$x=0.010$	50.2	(0.62,0.37)
$x=0.015$	63.6	(0.64,0.35)
$x=0.020$	100.0	(0.66,0.34)
$x=0.025$	34.1	(0.62,0.36)
$x=0.030$	59.7	(0.67,0.33)

Table 2. Experimental and calculated optical spectra (cm^{-1}) as well as the error (%) of europium at the potassium site of potassium tungstate phosphors.

Mult.	Calc.	Expt.	Error*	Mult.	Calc.	Expt.	Error*
$^7\text{F}_0$	0	0	0	$^5\text{D}_2$	21501	21231	1.3
$^7\text{F}_1$	202	208	2.9		21560	21522	0.2
	429				21599		
	430	431	0.2		21638		
$^7\text{F}_2$	782				21644		
	789			$^5\text{D}_3$	24309	24213	0.4
	1062				24349		
	1093	1097	0.4		24400		
	1594				24414		
$^7\text{F}_3$	1742				24435		

	1810				24447			
	2014				24453			
	2036				⁵ L ₆	24623		
	2148	2110	1.8			24672		
	2168					24887		
	2188					24944		
⁷ F ₄	2515					24990		
	2714					25106		
	2896					25197		
	2931					25264		
	3044					25414	25445	0.1
	3164					25595		
	3174	3167	0.2			25673		
	3202					25675		
	3574					25676		
⁷ F ₅	3636				⁵ L ₇	26139		
	3654					26229		
	3918					26318		
	3945					26328		
	3991					26348		
	4027					26359		
	4059					26383	26385	~0
	4198					26403		
	4573					26431		
	4651					26480		
	4661					26548		
⁷ F ₆	4837					26663		
	4885					26669	26667	~0
	5033					26733		
	5045					26808		
	5362				⁵ D ₄	26922		
	5393					26948		
	5458					26973		
	5493					27061		
	5502					27106		
	5641					27367		
	5667					27411	27473	0.2
	5946					27711	27701	~0
	5947					27795		
⁵ D ₀	17341	17331	0.1		⁵ H _j	31064	30675	1.3
⁵ D ₁	19064					31104		
	19136					31418		
	19149					31422	31447	0.1

*Error= $|E_{calc}-E_{expt.}|/E_{expt.}$