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Role of flux in the production process of red phosphors for white LEDs

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Abstract Eu^{3+}-doped potassium tungstate phosphor was synthesized by solid-state reactions. The as-produced phosphor was re-fired with a small amount of flux-like alkali carbonates and boron oxide. It was confirmed that the re-firing process containing a flux led to the uniform particle growth with smooth surface and improved Eu^{3+} distribution at the surface of particles, resulting in the enhanced red emission. The X-ray diffractometer (XRD) and X-ray photoelectron spectroscopy (XPS) analyses were used to determine the role of flux in the system.

Introduction

Since the light emitting diode (LED) was developed by Nakamura [1], it has attracted great attention in the area of solid-state lighting [2, 3]. Among several approaches for developing a white light source using an LED, the tricolor phosphor-based UV-LED is the most promising. In the tricolor phosphor-based UV-LED system, the phosphors are coated on the LED chip as a form of particles mixed with a resin. Three red, green, and blue phosphors used in this system absorb the near UV light from the UV-LED, generating white light.

There are factors to affect the luminescence properties of a phosphor, such as particle shape, size, surface, and homogeneity of composition. In general, the particles of spherical shape with uniform particle size of a few micrometers have the desirable luminescence properties like high brightness. Moreover, the defects in the phosphor act as detrimental factors to the luminescence. It has been known that a surface can be regarded as a two-dimensional (2-D) planar defect containing dangling bonds [4]. Therefore, the surface of the phosphor is a critical factor to the luminescence properties [5]. The presence of a surface causes a deviation from the typically ordered crystal structure, which leads to change in the luminescent characteristics. In general, the surface is often associated with non-radiative recombination and quenching of the luminescent mechanisms [6]. It has been known that the local variations in optical absorption and reflection losses caused by the surface roughness can deteriorate the luminescent intensity [4]. Even though surface roughness results in an increased luminescent efficiency in some cases [7], the smooth surface without defects increases luminescence brightness in most cases.

Inhomogeneous compositions lowering the luminescent efficiency of the phosphor have been observed in many systems. The differences in the vapor pressures of reactants might lead to inhomogeneous composition in the metal tungstate phosphor [8]. It is quite common for the surface composition of a powder particle to be different from that of its bulk. This is due to surface segregation, which is resulted from surface energy and strain effects [9]. Since the light of low energy used to excite the energy state of phosphor can penetrate just tens of nanometers into the crystal of phosphor, small difference in the compositions between the inner region and surface can give rise to a big difference in the luminescence properties.

In order to enhance the luminescence properties by controlling these factors, various synthetic processes have

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been used. The addition of flux in the solid-state reactions is one of the methods to improve the luminescence properties. The flux is defined as an inert high-temperature solvent to accelerate particle growth. Since the flux materials, such as oxides, halides, fluorides, and carbonates, usually have low melting points, they behave like a liquid phase to facilitate the particle growth.

In this study re-firing process containing a small amount of flux was employed in order to prevent the deterioration of luminescent properties due to the surface roughness and composition inhomogeneity. The Eu^{3+}-doped potassium tungstate phosphor was synthesized by solid-state reactions, followed by the re-firing process. In our earlier study, the Eu^{3+}-doped potassium tungstate phosphor was suggested as a red phosphor for white LEDs [10]. It was verified that the brightness of this phosphors was improved through the re-firing process. The role of various fluxes in the re-firing process was studied using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The reasons for the enhanced red emission obtained through the re-firing process will be focused in this work.

Experimental

$K_{4-3x}(WO_4)_2{:}Eu^{3+}{}_x$ phosphor (KWE_x) was synthesized by solid-state reactions. As starting materials, K_2CO_3, WO_3, and Eu_2O_3 (Kojundo Chemical Lab Co., 99.9%) were used. Stoichiometic amounts of reactants were mixed by ball-milling for 10 h. The weight ratio of zirconia balls and powder was 60:1 and acetone was used as a medium. After drying at 80 °C for 24 h, the mixture was fired in a box furnace at 800–1,000 °C for 0–3 h. The as-produced powder was re-fired at 800–1,000 °C for 0–3 h with a small amount of flux, which is chosen among Li_2CO_3, Na_2CO_3, K_2CO_3, and B_2O_3. The amount of a flux was varied in the range of 0.5–5.0 wt.%. The flux was mixed with the as-produced powder using the mortar. The re-fired powder was soaked in warm water and the flux was removed by vigorous stirring. Then, the powder was collected from the solution by centrifugation and the dry powders were subjected to various analyses. In order to optimize the synthetic conditions for the KWE phosphor, the composition of KWE phosphor was fixed to the $K_{1.6}(WO_4)_2{:}Eu^{3+}_{0.8}$ ($KWE_{0.8}$), which was reported as the most efficient composition in our earlier research [10].

Powder morphology was observed by scanning electron microscope (SEM, JSM-6360, JEOL, Japan). Excitation and emission spectra were measured at room temperature using a spectrofluorometer (JASCO, FP-6500, Japan). For the changes in the crystalline structure and phase with increasing temperature, a X-ray diffractometer (XRD, M18XHF-SRA, MAC Science Co., Yokohama, Japan) and a differential temperature analyzer (DTA, DSC910S, TA Instrument, USA) were used. X-ray photoelectron spectroscopy (XPS, Axis, Kratos, Japan) was performed to determine the binding state and composition in the surface of the particles.

Results and discussion

Optimization of synthetic conditions

The KWE phosphor produced by solid-state reactions exhibited a strong absorption of near UV light and red emission. The excitation spectrum of Fig. 1 shows that the $KWE_{0.8}$ phosphor has sharp excitation peaks in the near UV to green region, which is attributed to the intra-configurational 4*f*-4*f* electron transitions of Eu^{3+}. Due to the strong absorption in the near UV to green region, the KWE phosphor would have high-emission efficiencies in a phosphor-based UV-LED lighting system. When excited by 396 nm corresponding to the $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+}, the $KWE_{0.8}$ phosphor resulted in strong red emission peaks as shown in Fig. 1. Since the surrounding of the Eu^{3+} ions in the host materials has no inversion symmetry, emission peaks due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} dominates [10, 11]. When the as-produced $KWE_{0.8}$ phosphor was re-fired at 900 °C for 2 h with 1 wt.% B_2O_3, the emission intensity of the re-fired $KWE_{0.8}$ phosphor was enhanced without any change in the emission spectrum shape.

In order to find out the optimum synthetic conditions for the KWE phosphor, DTA and XRD analyses were conducted. The DTA result in Fig. 2a indicates that some reactions occur at 820 °C and 980 °C. The XRD results in Fig. 2b show that the undesired phases such as K_2WO_4 and $Eu_2(WO_4)_3$ form at temperatures below and above 900 °C, respectively. Based on the results of DTA and XRD analyses, it is confirmed that the K_2WO_4 and $Eu_2(WO_4)_3$

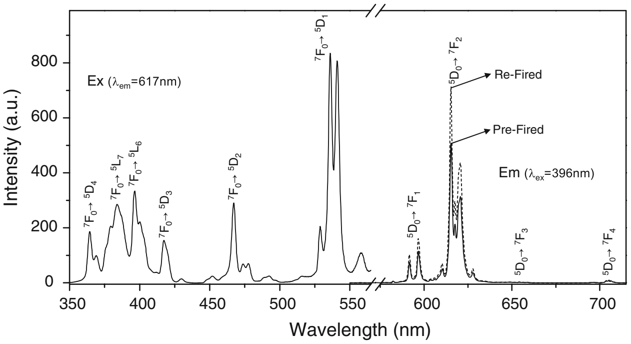

Fig. 1 Excitation and emission spectra of the $KWE_{0.8}$ phosphor re-fired at 900 °C for 2 h with 1 wt.% B_2O_3 after pre-fired at 900 °C for 2 h

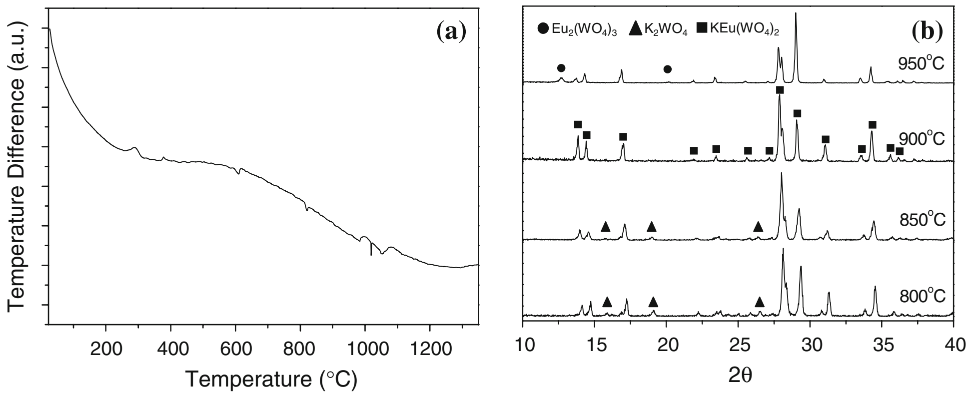

Fig. 2 (**a**) DTA result of the mixture of starting materials and (**b**) XRD results of the $KWE_{0.8}$ phosphors heat-treated at different temperatures for 2 h

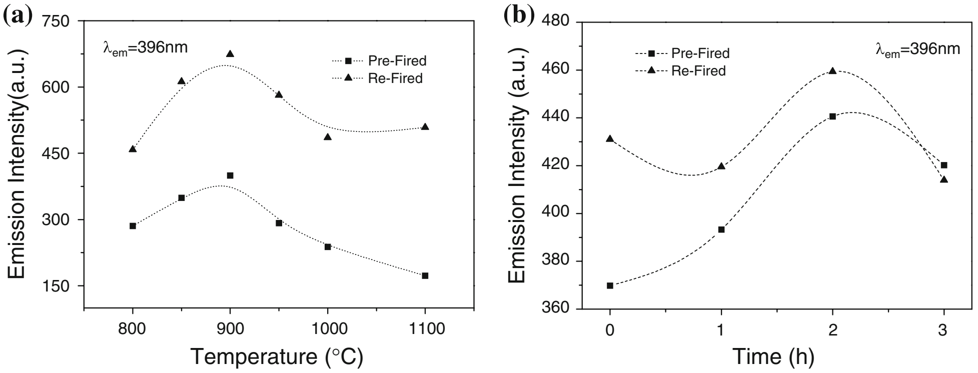

Fig. 3 Emission intensities of the $KWE_{0.8}$ phosphors pre-fired and re-fired (**a**) at different temperatures for 2 h and (**b**) at 900 °C for different times. 1 wt.% B_2O_3 was used as flux in the re-firing process

phases form favorably at temperatures lower than 820 °C and higher than 980 °C, respectively. Therefore, the pure KWE phosphor is expected to form in the temperature range of 820–980 °C.

Figure 3a and b show that the emission intensity of the $KWE_{0.8}$ Phosphor depends on the firing temperature and time. As expected from the DTA and XRD results, the $KWE_{0.8}$ phosphor produced at 900 °C for 2 h had the strongest emission intensity. When the as-produced powder is re-fired with 1 wt.% B_2O_3, the optimum condition for the re-firing process is 900 °C for 2 h. Figure 4 shows the emission intensities of the $KWE_{0.8}$ phosphors pre-fired at 900 °C for 2 h and re-fired at 900 °C for 2 h with different amounts of fluxes such as K_2CO_3 and B_2O_3. The amounts of the fluxes were varied between 0.5 and 5.0 wt.%. When the as-produced powder was re-fired with 1 wt.% of flux, the emission intensity was the strongest.

The relative emission intensities of the $KWE_{0.8}$ phosphors re-fired with various fluxes are listed in Table 1. The re-fired $KWE_{0.8}$ phosphors exhibited an increase in emission intensities compared to the pre-fired one. Of various fluxes B_2O_3 was the most effective. The effectiveness of the fluxes on the luminescence was determined by re-firing the phosphor without any flux. The phosphor re-fired without a flux had the emission intensity stronger than the as-produced one, confirming the effective role of flux.

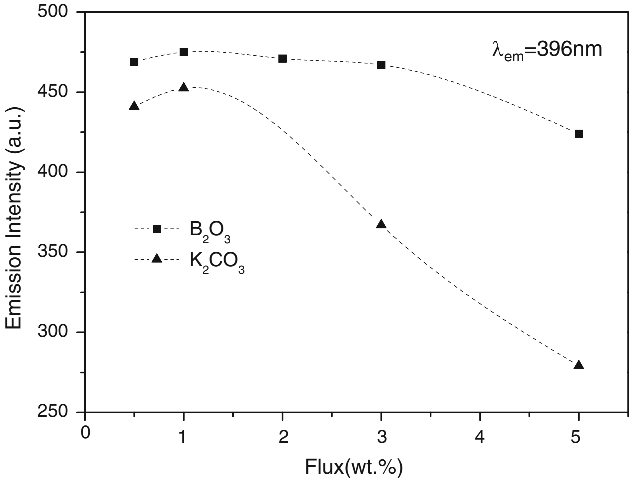

Fig. 4 Emission intensities of the $KWE_{0.8}$ phosphors pre-fired at 900 °C for 2 h and re-fired at 900 °C for 2 h with different amounts of fluxes

Roles of flux

The SEM images of Fig. 5 show that flux accelerates the growth of phosphor particles. The pre-fired phosphor has a particle size smaller than 5 μm with rough surface while the re-fired powders bring the size up to 15–20 μm along with smooth surface. In case of the powder re-fired without

Table 1 Relative emission intensities of the $KWE_{0.8}$ phosphors pre-fired at 900 °C for 2 h and re-fired at 900 °C for 2 h with various fluxes of 1 wt.%. In the relative emission intensity (I/I_o), I_o is the emission intensity of the pre-fired $KWE_{0.8}$ phosphor

Flux	Relative emission intensity (I/I_o)
No flux	1.148
Li_2CO_3	1.307
Na_2CO_3	1.261
K_2CO_3	1.235
B_2O_3	1.397

flux, the particle growth is not uniform as shown in Fig. 5b. When Li_2CO_3, Na_2CO_3, and K_2CO_3 are used as fluxes, the particle sizes are more uniform compared to the powder re-fired without flux. However, a small amount of particles smaller than 1 μm are also observed. On the other hand, the addition of B_2O_3 led to the uniform particle growth as shown in Fig. 5f. The enhanced emission intensities of the $KWE_{0.8}$ phosphors re-fired with fluxes must be attributed to the uniform particle growth and smooth surface. Since, however, the $KWE_{0.8}$ phosphor re-fired without a flux also provides the smooth surface, the enhanced intensity cannot be explained solely by the particle uniformity and surface condition.

The improved luminescence of such phosphors have been explained in terms of a substitutional effect and charge compensation of flux [12, 13]. In order to find the changes in the surface compositions of the KWE particles during re-firing process, XPS analyses were carried out. The XPS result in Fig. 6 indicates that the compositional changes occurred in the surface of the $KWE_{0.8}$ particles during the re-firing process. Since the penetration depth of laser beam used in the XPS analysis is tens of nanometers, the atomic ratio obtained from the XPS results can be taken as the surface composition of the $KWE_{0.8}$ particles.

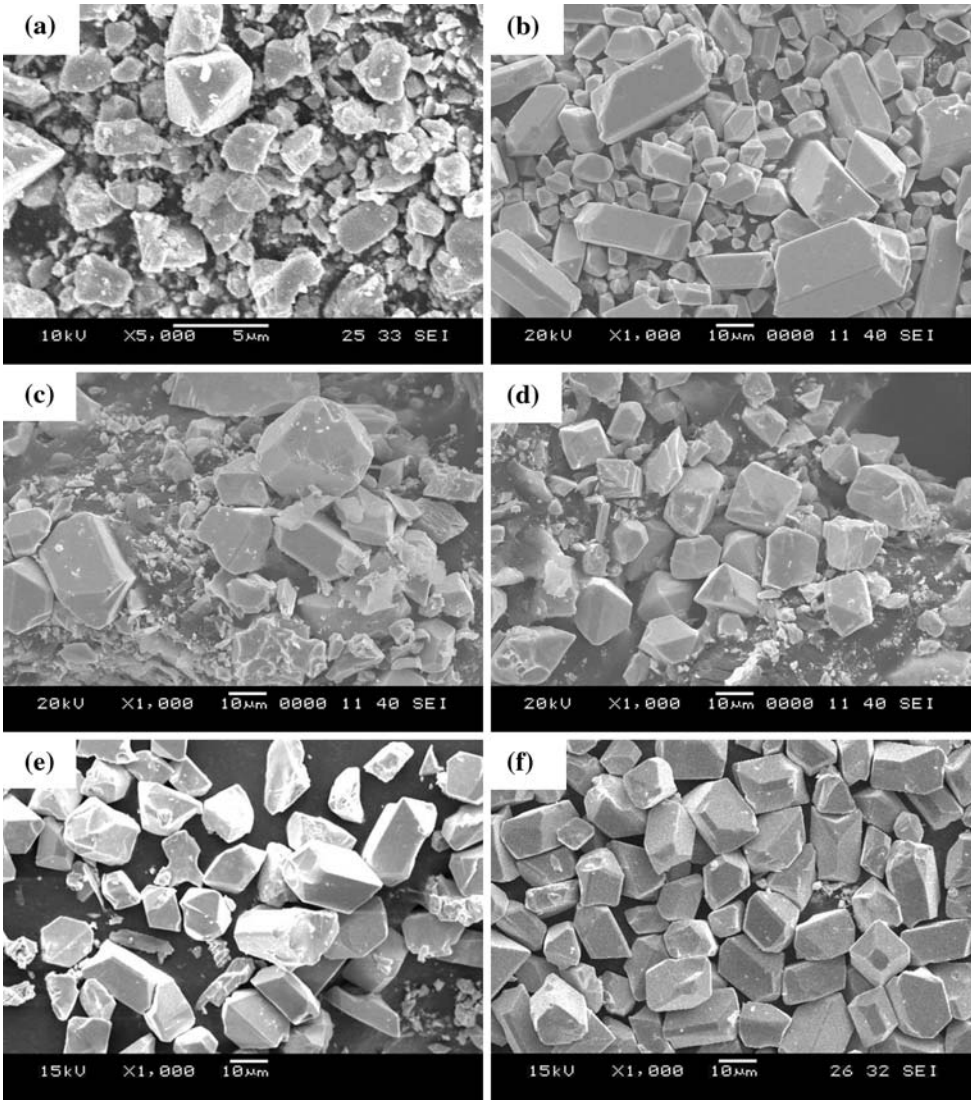

Fig. 5 SEM images of the $KWE_{0.8}$ phosphors (**a**) pre-fired at 900 °C for 2 h and re-fired at 900 °C for 2 h with (**b**) no flux, (**c**) Li_2CO_3, (**d**) Na_2CO_3, (**e**) K_2CO_3, and (**f**) B_2O_3 of 1 wt.%

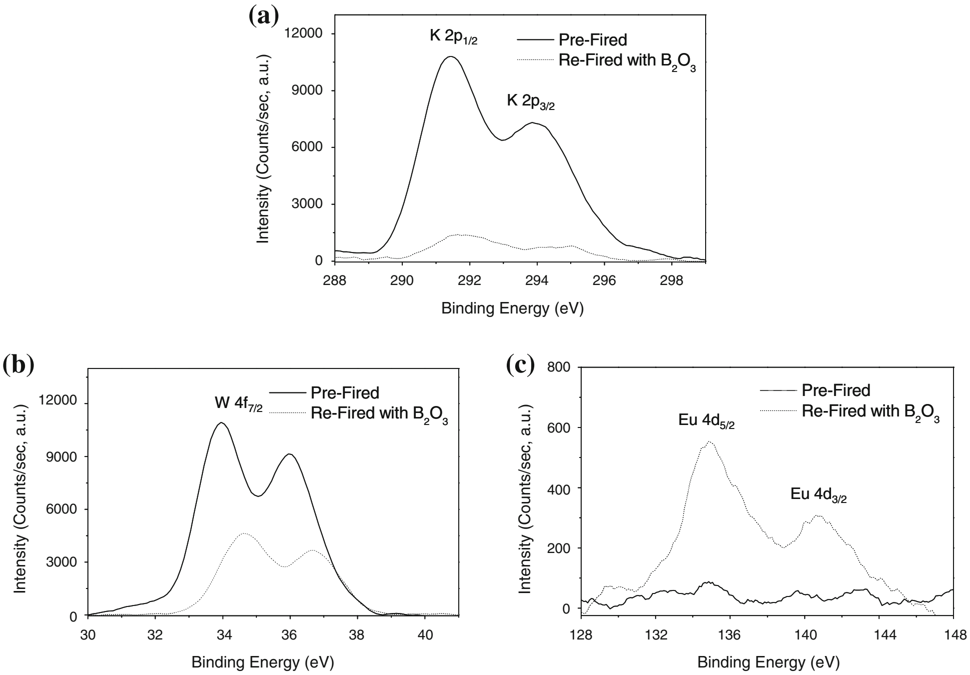

Fig. 6 XPS spectra from (**a**) K 2p, (**b**) W 4f, and (**c**) Eu 4d of the $KWE_{0.8}$ phosphor pre-fired at 900 °C for 2 h and re-fired at 900 °C for 2 h with B_2O_3 of 1 wt.%

When the $KWE_{0.8}$ phosphor was re-fired with 1 wt.% B_2O_3, K $2p_{3/2}$, and K $2p_{1/2}$ peaks became low and undistinguishable as shown in Fig. 6a, implying a change in the chemical environment of cation. In Fig. 6b, W $4f_{7/2}$ peaks at 34 eV and 36 eV are assigned to the peaks due to W metal and MWO_4 ($M = Co, Cu$), respectively [14, 15]. Since $4f_{7/2}$ peak shifts to the higher binding energy as W^{3+} ions strengthen the bond with oxygen [16], it can be inferred that the re-firing process leads to stronger W–O bindings. In Fig. 6c, there are two peaks for Eu $4d_{5/2}$ at 135 eV and Eu $4d_{3/2}$ at 141.5 eV [17], confirming that europium does not exist in the form of Eu^{2+}, but of Eu^{3+}. The increased intensities of the Eu $4d_{5/2}$ and Eu $4d_{3/2}$ peaks after the re-firing process imply that the concentration of the Eu^{3+} ions in the surface of particles is increased. It is likely that Eu^{3+} ions diffuse from the inner region to the surface of particles. It was reported previously that boron oxide has a substitutional effect of boron ions even at low concentrations [12]. However, boron was not detected by XPS analysis of this study.

The quantitative analyses of the XPS spectra in Table 2 show the changes in the surface composition more clearly. In case of the pre-fired particles, a large amount of potassium is present at the surface of particles while no europium is found. This might be due to the surface segregation of potassium. The surface segregation of the constituents of a phosphor results from the surface energy and strain in the matrix [9]. The surface segregation of atoms with radii larger than the other atoms in the host lattice would release the matrix strain.

Thus, K^+ ion (1.65Å in 8-coordinated dodecahedron), which is larger than Eu^{3+} ion (1.206Å in 8-coordinated dodecahedron), can segregate to the phosphor surface. It is to be noted that the amount of europium increases at the surface with a decrease in potassium after re-fired with various fluxes. The atomic ratio at the surface of the particles, when re-fired with a flux, becomes similar to the theoretic ratio of the $KWE_{0.8}$ phosphor. On the other hand, europium is not present at the surface of the $KWE_{0.8}$ particles when re-fired with no flux. As shown in Tables 1 and 2, the relative emission intensity (I/Io) becomes improved if the atomic ratio at the surface is close to the theoretic one. Therefore, it is certain that the enhanced emission intensities in the $KWE_{0.8}$ phosphors re-fired with fluxes are largely attributed to the increased amount of europium at the surface.

Figure 7 shows a schematic for the particle growth during re-firing process. At the temperatures above the melting point of flux, the molten flux would form a thin layer on the surface of the particles as shown in the figure. It makes it possible for the europium ions to diffuse out to the surface, spreading out with the help of flux. Thus, we conclude that the flux facilitates uniform growth of the phosphor particles and distribution of europium through easy transport. The path for the europium transport should be particle boundaries, which could be penetrated by molten phase. In general the re-firing of the KWE phosphor with flux is expected to enhance emission intensity.

Table 2 Quantitative analyses of the XPS results in the $KWE_{0.8}$ phosphor pre-fired at 900 °C for 2 h and re-fired at 900 °C for 2 h with various fluxes

Process	Peak	Binding energy (eV)	FWHM (eV)	Raw height (Counts/s)	Atomic ratio (K:W:Eu:O)
Pre-fired	K 2p	292.25	4.435	2684.1	4.67:2:0.00:16.31
	W 4f	34.65	3.676	2815.6	
	O 1 s	529.45	3.255	4200.3	
	Eu 4d	–	–	–	
Re-fired without flux	K 2p	292.36	2.57	249.4	1.39:2:0.00:10.96
	W 4f	35.16	1.784	880.1	
	O 1 s	529.56	3.038	882.2	
	Eu 4d	–	–	–	
Re-fired with Li_2CO_3	K 2p	295.72	4.301	193.9	1.26:2:0.57:17.25
	W 4f	35.32	4.01	757.3	
	O 1 s	529.82	3.195	1194.3	
	Eu 4d	136.72	1.152	134.8	
Re-fired with Na_2CO_3	K 2p	292.72	2.016	227.7	0.93:2:0.30:12.68
	W 4f	35.42	1.853	1198.4	
	O 1 s	530.12	2.304	1390.1	
	Eu 4d	135.67	1.164	113.7	
Re-fired with K_2CO_3	K 2p	292.25	4.352	193.6	2.50:2:0.82:38.84
	W 4f	37.725	3.831	379.7	
	O 1 s	530.15	3.4	1349.8	
	Eu 4d	136.45	1.339	97.1	
Re-fired with B_2O_3	K 2p	292.25	2.281	368.6	1.14:2:0.49:17.46
	W 4f	35.225	3.604	1576.4	
	O 1 s	529.95	2.512	2517.4	
	Eu 4d	135.05	2.691	242.7	

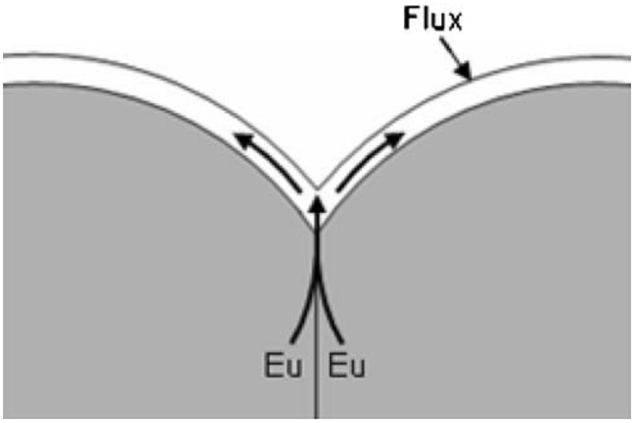

Fig. 7 A schematic diagram showing the diffusion of europium from the inner region to the surface of particles during coalescence

Conclusions

As a method to improve the luminescence properties of the Eu^{3+}-doped potassium tungstate phosphor, the re-firing process with flux was employed. This study shows that flux induces uniform distribution of europium at the phosphor particles, resulting in improved luminescence. The presence of molten flux in the re-firing process also leads to uniform particle growth along with smooth surface. It should be noted that the composition at the surface of KWE particles, which determines the emission intensity, changes differently depending on the flux used in the re-firing process.

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