

## Mild Hydrothermal Synthesis and Optical Properties of the Complex Fluoride $\text{KMgF}_3$ Doped with Eu

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**Abstract:**  $\text{KMgF}_3$  doped with Eu was synthesized by mild hydrothermal method at 240°C for the first time. The excitation and emission spectra of the  $\text{KMgF}_3 : \text{Eu}^{2+}$  phosphor were measured. Comparing with the sample synthesized through solid state reaction, the variation in the excitation spectra at 360 nm resulted from the existences of  $V_K$  color centers; the low emission intensity was due to  $\text{Eu}^{2+}$  having transferred part energy to  $V_K$  color centers.

**Keywords:** Mild hydrothermal synthesis, complex fluoride, optical properties, europium (II).

Perovskite complex fluorides have attracted great interests due to their particular physical properties such as antiferromagnetic characteristics<sup>1</sup>, photoluminescence behavior<sup>2</sup>. Complex fluorides are usually prepared by solid state reactions at high-temperature. In spite of inert atmosphere, it is inevitable to contain a bit of oxygen. This has great effect on the luminescent character of rare earth ions. There are also reports about synthesizing some binary fluorides by high-temperature hydrothermal method above 400°C<sup>3</sup>, but this requires complicated experimental apparatus and technology. In recent years, Feng *et al.*<sup>4</sup> have synthesized a series of complex fluorides by the hydrothermal method which has the advantages of pure phase, low content of oxygen and mild synthesis conditions. Whether the optical properties of the rare earth doping samples, synthesized by hydrothermal in mild condition and at high-temperature are identical? It was no report in literature yet. In this paper, we reported the synthesis of  $\text{KMgF}_3$  phosphor with doping Eu by both above-mentioned methods, their spectra analysis and the discussion of the differences were also presented.

### Experimental

The initial materials KF,  $\text{MgF}_2$  (A. R) were fired for several hours at the atmosphere of high-pure  $\text{N}_2$  at 500°C.  $\text{EuF}_3$  was prepared from high-pure  $\text{Eu}_2\text{O}_3$  (99.99%). Each component was weighed precisely according to the chemical stoichiometric ratio and mixed, then the deionized water was added to 70-80 percent of the whole capacity. The

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reaction mixture was sealed in a teflon-lined stainless-steel autoclave and heated at 240°C under autogenous pressure for 1 d. After the autoclave was cooled, the final powder product was washed with deionized water and dried in air at room temperature. The sample of  $\text{KMgF}_3 : \text{Eu}$  was synthesized at high-temperature in solid state reaction according to literature<sup>6</sup>.

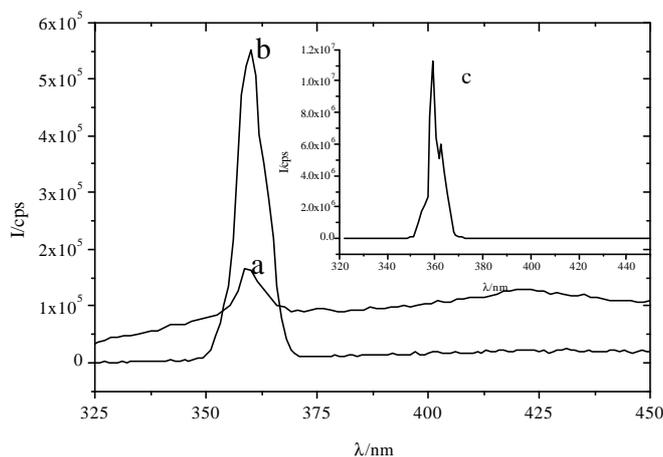
The excitation and emission spectra were measured with a SPEX Fluorolog spectra-fluorometer. Each element component was characterized by ICP-AES method.

### Results and Discussion

**Figure 1** demonstrated the emission spectra of  $\text{KMgF}_3 : \text{Eu}$  at room temperature synthesized by mild hydrothermal method (**Figure 1a, b**) and at high-temperature in solid state reactions (**Figure 1c**). The emission spectra (**Figure 1a**) of  $\text{KMgF}_3 : \text{Eu}$  consisted of a sharp peak which was ascribed to the  ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$  transition of  $\text{Eu}^{2+}$  and a broad band transition with a maximum at 422 nm. **Figure 1c** showed only an emission peak of  ${}^6\text{P}_J \rightarrow {}^8\text{S}_{7/2}$  transitions of  $\text{Eu}^{2+}$ .

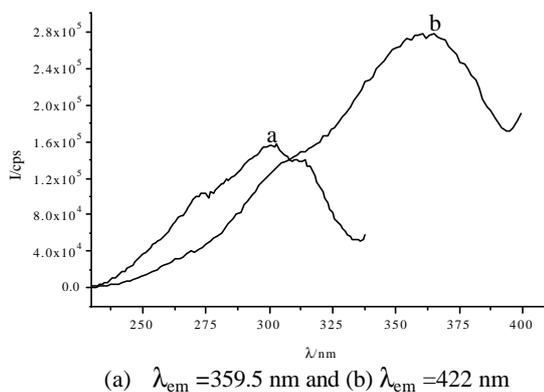
The excitation spectra of  $\text{Eu}^{2+}$  emission ( $\lambda_{\text{em}}=359.5$  nm and 422 nm) of  $\text{KMgF}_3 : \text{Eu}$  (hydrothermal synthesis) were also measured (**Figure 2**). In the excitation spectra (**Figure 2a**) of 359.5 nm emission, there was a broad band peak with a maximum at 302 nm, which might be resulted from  ${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}_{7/2}$ . But in the 422 nm emission excitation spectra (**Figure 2b**), except the broad band peak of  $\text{Eu}^{2+}$  at 310 nm, there was a very strong broad band peak at 360 nm.

**Figure 1** The emission spectra of  $\text{KMgF}_3 : \text{Eu}^{2+}$  by hydrothermal synthesis



- (a) annealing before;
- (b) annealing later;
- (c) the high-temperature sample.

**Figure 2** The excitation spectra of  $\text{KMgF}_3:\text{Eu}^{2+}$  (hydrothermal synthesis)



It means there were different luminescence centers. The broad band emission at 360 nm was caused by existing color centers. After annealing process, the disappearance of the emission peak at 422 nm (**Figure 1b**) showed that the color centers existed indeed. As far as we know, there might exist three kinds of possible color centers caused by  $\text{O}^{2-}$ , F or the vacancy of  $\text{K}^+$ . The reference<sup>4</sup> proves that the content of oxygen in  $\text{KMgF}_3$  is very low, so the possibility of  $\text{O}^{2-}$  causing the color centers might be negligible.

From the excitation spectra, the range of the excitation peak of the color centers was from 325 nm to 385 nm. According to reference<sup>7</sup>, excitation peaks of three color centers in  $\text{KMgF}_3$  are:  $\text{F}_2$  (282, 445 nm),  $\text{F}_3$  (250, 395 nm) and  $\text{V}_\text{K}$  (340 nm), so the existence of  $\text{F}_2$ ,  $\text{F}_3$  color centers in our excitation spectra could be eliminated. The excitation position of  $\text{V}_\text{K}$  color centers at 340 nm was included in the spectra scope, so the broad band peak of the hydrothermal synthesis sample should result from  $\text{V}_\text{K}$  color centers. Meanwhile, Tsuboi *et al.*<sup>8</sup> also proved that just because of the existing of  $\text{K}^+$  vacancy, the different displacement sites of  $\text{Eu}^{2+}$  substituting for  $\text{K}^+$  was observed.

From **Figure 1**, it can also be seen, the emission intensity of  $\text{Eu}^{2+}$  in hydrothermal sample was lower than that in high-temperature sample about two orders of magnitude. In order to find out the reason, we carried out component analysis, and the results showed that the content of  $\text{Eu}^{2+}$  in high-temperature (3.5 mg/g) and hydrothermal (3.9 mg/g) samples were nearly equal. Analyzing the relic solution of the hydrothermal sample, the amount of  $\text{Eu}^{2+}$  was  $1.25 \times 10^{-5}$  mg/g, which could be neglected. The result showed that most of  $\text{Eu}^{2+}$  in the hydrothermal sample had entered into the sites. But what the reason of causing the weak luminescence (**Figure 1a**) is not clear. By analyzing **Figure 1** and **Figure 2**, there were good overlaps between excitation position of  $\text{V}_\text{K}$  color centers and the line emission of  $\text{Eu}^{2+}$ ,  $\text{Eu}^{2+}$  might transfer its energy to  $\text{V}_\text{K}$  color centers and cause to lower the line emission intensity of  $\text{Eu}^{2+}$  itself. After the sample  $\text{KMgF}_3 : \text{Eu}$  (synthesized by mild hydrothermal method) was annealed (**Figure 1b**), the emission peak at 422 nm disappeared, while the intensity of the emission peak at 359.5 nm increased obviously, this also showed the existence of energy transfer from  $\text{Eu}^{2+}$  to  $\text{V}_\text{K}$  color centers.

In summary, the peak at 360 nm in hydrothermal samples resulted from  $\text{V}_\text{K}$  centers.

The energy transfer from  $\text{Eu}^{2+}$  to  $\text{V}_\text{K}$  centers occurred.

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