

# Study of Color Centers and Trace Oxygen in $\text{KMgF}_3\text{:Eu}$ Single Crystal

Haiquan Su, Zhihong Jia, and Chunshan Shi\*

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, China, 130022

Received July 3, 2001. Revised Manuscript Received September 17, 2001

Using the Bridgman–Stockbarger method, the  $\text{KMgF}_3\text{:Eu}^{2+}$  single crystal was grown. The color centers in unirradiated  $\text{KMgF}_3\text{:Eu}$  crystal were studied. By thermal annealing, we confirmed the 422-nm emission resulted from color centers and oxygen centers, and we proved the energy transfer from  $\text{Eu}^{2+}$  to color centers. From spectra, the relative oxygen content in crystal was calculated, and the relationships of oxygen displacing fluorine were studied.

## Introduction

$\text{KMgF}_3$ , which was a typical cubic perovskite structure, was ideal material for searching for a new solid-state laser because of several advantages: good homogeneous optics, high thermal stability, low melting point, anisotropy, high optical transparency, and so forth. Because of the broad, forbidden band and the weak crystal field intensity,  $\text{KMgF}_3$  could stabilize low-valence, rare-earth ions, which could be used to further refine spectra structure of these rare-earth ions. An obvious example was that the line emission of the  $f-f$  transition of the  $\text{Eu}^{2+}$  was observed in  $\text{KMgF}_3\text{:Eu}$ . Riley et al.<sup>1,2</sup> studied the color center of the irradiated  $\text{KMgF}_3$  crystal (the impurity concentration was lower than  $10^{-3}$  mol %) by polarized bleaching experiments and identified the absorption and emission locations of  $\text{F}$ ,  $\text{F}_2$ ,  $\text{F}_3$ , and  $\text{V}_\text{K}$  color centers. Gektin et al.<sup>3,4</sup> studied the dependence of the color center on temperature and the effect of oxygen impurity on irradiated materials. However, the clarification of the complex emission bands in the region of 370–700 nm is still unclear. In this paper, we conducted several experiments to study the color centers and oxygen centers in the unirradiated  $\text{KMgF}_3\text{:Eu}$  single crystal. Furthermore, the oxygen content and the substitution process between O and F in the crystal were studied.

## Experimental Section

The  $\text{KMgF}_3\text{:Eu}$  single crystal was grown by vertical Bridgman method in graphite crucible at Ar atmosphere. The initial materials of KF and  $\text{MgF}_2$  were fired under high purity Ar atmosphere at 120 °C to remove the trace water, and  $\text{EuF}_3$  was prepared by  $\text{Eu}_2\text{O}_3$  (99.99%) using the method as reported

by the literature.<sup>5</sup> All reactants were analytical grade. The crucible was lowered at the speed of 4.23–4.90 mm/h, and the temperature was kept at 1125 °C during the growth. After 12 h, the lowering crucible was stopped and the temperature was decreased to 240 °C at the speed of 1 °C/min, then the crystal was allowed to cool to room temperature. The crystals were transparent. Polished pieces of  $5 \times 6 \times 7$  mm size were used for the measurements.

Absorption spectra were obtained with a Model 8452A diode array spectrophotometer. High-resolution emission spectra were recorded using a Spex model 1403 double monochromator equipped with a Spex model DM1B controller and a Hamamatsu R928 photomultiplier tube. Excitation wavelengths at 350.9 and 337.5 nm were provided by a coherent Model Innova-100-K3 Krypton ion laser.

The low-resolution fluorescence spectra were obtained by Spex-FL-2T2 fluorescence spectrophotometer equipped with 0.22-nm Spex Model double 1680 monochromator. The diffuse reflectance spectra were recorded on Perkin-Elmer 320 scanning spectrometer equipped with a Hamamatsu integrating sphere attachment. For these measurements, a plain KBr was used as a blank, and finely ground  $\text{BaSO}_4$  was used as a reference. The spectra were recorded in the transmittance mode and then numerically Kubelka–Munk corrected using the facilities of Spectra Calc software.

For lifetime measurements, a frequency doubled-dye laser (Lambda Physik Scanmate 2E), operating on Rhodamine 101 dye and pumped by the second harmonic of a Nd:YAG laser operating at 10 Hz, was used as the excitation light source. After frequency doubling, this dye laser generates light pulses of about 3-mJ total energy at wavelength of 308 nm, the spectral bandwidth is about  $0.05 \text{ cm}^{-1}$  (fwhm) in a Gaussian envelope.

## Results and Discussion

Figure 1 was the emission spectrum of the  $\text{KMgF}_3\text{:Eu}^{2+}$  crystal at different laser excitations. As can be seen, the overall appearance of the spectra consisted of complex emission bands in the range of 370–700 nm and varied with different exciting wavelengths. When the exciting wavelength was 350.9 nm, the emission at 402, 470, and 590 nm were observed (Figure 1a).

The emission spectrum excited at 312 nm is shown in Figure 2a. Besides the sharp line emission at 360 nm

\* To whom correspondence should be addressed. E-mail: cshi@ciac.jl.cn. Fax: +86-431-5685653.

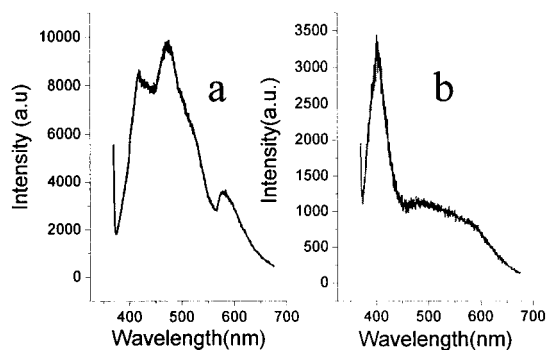
(1) Riley, C. R.; Sibley, W. A. *Phys. Rev. B* **1970**, *1*, 2789.

(2) Riley, C. R.; Yun, S. I.; Sibley, W. A. *Phys. Rev. B* **1972**, *5* (8), 3285.

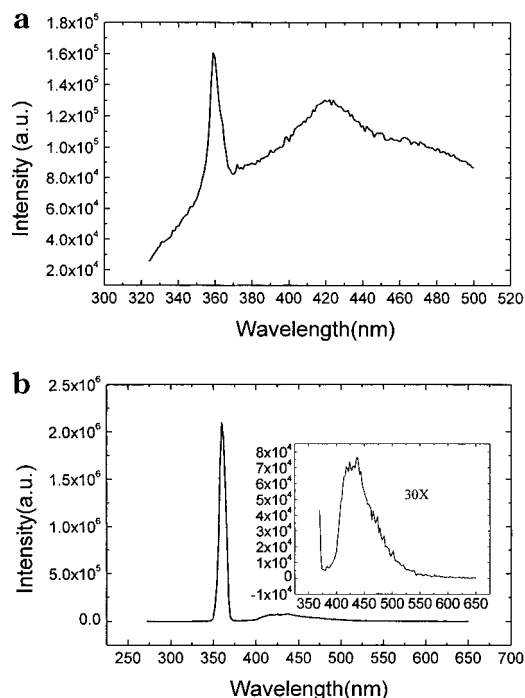
(3) Gektin, A. V.; Komar, V. K.; Shiran, N. V.; Shlykhturov, V. V.; Nesterenko, N. P.; Krasovitskaya, I. M.; Kornienko, V. V. *IEEE Trans. Nucl. Sci.* **1995**, *42*, 311.

(4) Gektin, A. V.; Krasovitskaya, I. M.; Shiran, N. V. *J. Lumin.* **1997**, *72–74*, 664.

(5) Shi, C.; Ye, Z.; Takahashi, K. *J. Chem. Soc. Jpn.* **1985**, *2*, 152.



**Figure 1.** Emission spectra of  $\text{KMgF}_3: \text{Eu}^{2+}$  excited with laser at room temperature, (a) 350.9 nm (b) 337.5 nm.



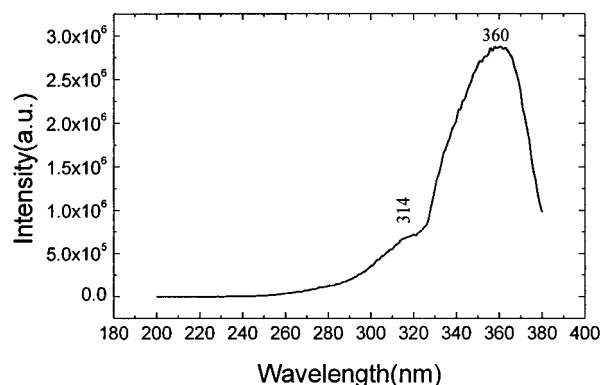
**Figure 2.** (a) Emission spectra of  $\text{Eu}^{2+}$  in  $\text{KMgF}_3: \text{Eu}^{2+}$  at 312 nm excitation (anneal before). (b) Emission spectra of  $\text{Eu}^{2+}$  in  $\text{KMgF}_3: \text{Eu}^{2+}$  at 312 nm excitation (anneal after).

**Table 1. Variation of Band/Line Ratio of  $\text{KMgF}_3: \text{Eu}^{2+}$  with Different Excited Power**

excited line	356.4	354.5	350.9	337.5
power (mw)	14	10	20	1.5
$I_b/I_l^a$	4.5	2.7	17	5.7

<sup>a</sup> The ratio of integral intensity of the 370–670-nm band emission and the 359-nm line emission of  $\text{Eu}^{2+}$ .

(arising from  $f-f$  transition of  $\text{Eu}^{2+}$ ), a broad-band emission appeared at 402 nm, which resulted from two possible centers: the one was the color center and the other was the trace oxygen in crystal. If the emissions at 402, 420, 470, and 590 nm came from color centers, the emission intensity should increase under UV irradiation. In Table 1, the values of the integral intensity ratio of the band to line increased with the increased irradiated power, which indicated that the emission at 370–700 nm resulted from the color center. According to the literature,<sup>2</sup> the emission at 470 nm can be attributed to the  $F_3$  center, while the emission at 590 nm can be attributed to the  $F_2$  center. No corresponding attribution for the emission at 402 and 420 nm was reported. To further confirm the emission at 420 nm



**Figure 3.** Excitation spectra of  $\text{Eu}^{2+}$  in  $\text{KMgF}_3: \text{Eu}^{2+}$  ( $\lambda_{\text{em}} = 420$  nm).

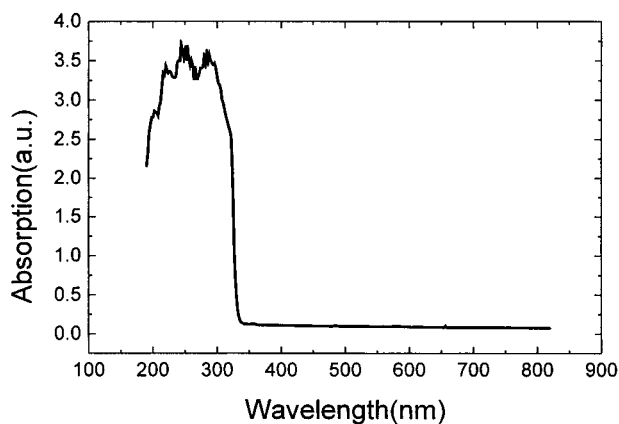
coming from the color center, we performed an annealing process at 500 °C (Figure 2b). Comparing Figure 2b with Figure 2a, we found that the emission intensity at 420 nm in the annealed crystal was about 30 times lower than in the unannealed sample. However, the weak emission at 420 nm could still be seen, which was attributed to the trace oxygen in the  $\text{KMgF}_3: \text{Eu}$  crystal. Because KF could easily absorb water from atmosphere and hydrolyze at high temperature, it was extremely difficult to avoid trace oxygen in the crystal-grown process.<sup>4</sup> There were two possible mechanisms for the decreased amount of color centers during the annealing process. One was that in the process of heating, the color centers were partially transformed from  $F$  to  $F_n$  and their quantity was decreased. Another was that  $\text{Eu}^{2+}$  acted as the recombination center of electron vacancy in lattice to suppress the formation of the  $F$  center. With the increasing of annealing temperature, the vacancy mobilized, and the recombining ability between interstitial-vacancy pairs strengthened, which resulted in the decrease of the emission intensity.

Comparing Figure 2a with Figure 2b, we found that the emission intensity at 360 nm in the annealed sample increased. The value was about 8.4 times larger than in the unannealed sample. The excitation spectrum of 420 nm was shown in Figure 3. The peak value at maximum intensity of the color center was at 360 nm, which overlapped the maximum peak value of  $f-f$  transition emission of  $\text{Eu}^{2+}$ . Thus on the basis of the energy transfer theory,<sup>6</sup> the energy transfer from the  $f-f$  transition emission of the  $\text{Eu}^{2+}$  to the color centers happened in this system. After the color center was removed by annealing, the emission intensity at 360 nm increased accordingly.

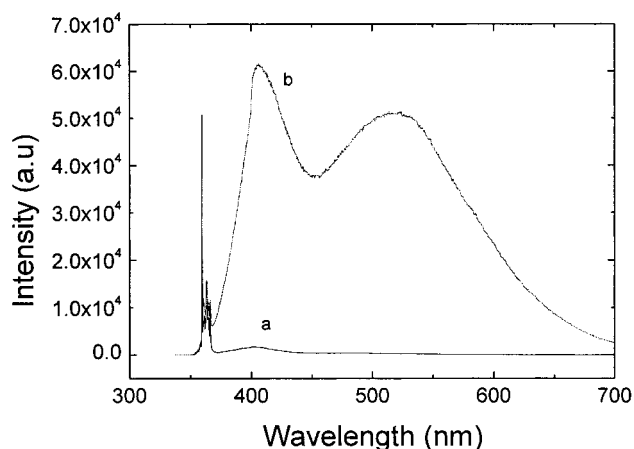
As described above, the trace oxygen was inevitable in the crystal-grown process. The absorption spectrum of  $\text{KMgF}_3: \text{Eu}^{2+}$  (1 mol %) at 300 K is shown in Figure 4. Four absorption peaks at 197, 221, 250, and 287 nm can be seen. The 197- and 221-nm bands were attributed to the absorption of the trace oxygen in the crystal,<sup>3,7</sup> and the 250- and 287-nm bands resulted from  $\text{Eu}^{2+}$ . To estimate the relative content of oxygen in samples, we fitted the adsorption curve in the range of 190–350 nm using the Lorenz function. It is given in Table 2.

(6) Dexter, D. L. *J. Chem. Phys.* **1959**, *21*(5), 838.

(7) Gektin, A. V.; Komar, V. K.; Shlyahurov, V. V.; Shiran, N. V. *IEEE Trans. Nucl. Sci.* **1996**, *43* (3), 1295.



**Figure 4.** UV-vis absorption spectra of  $\text{KMgF}_3\text{:Eu}^{2+}$  (bottom layer) at 300 K.

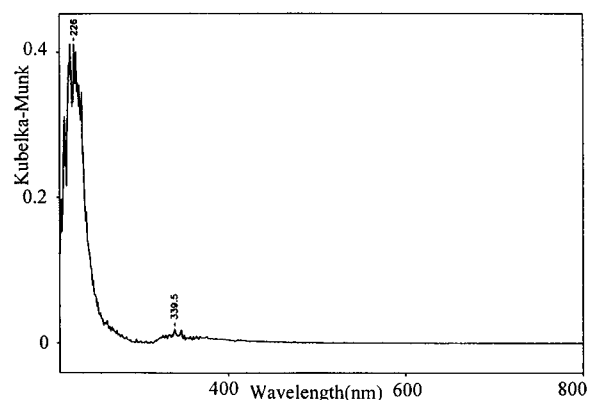


**Figure 5.** Emission spectra of  $\text{KMgF}_3\text{:Eu}^{2+}$  at 337.5-nm laser excitation. (a) crystal (b) ground powder.

**Table 2. Oxygen Content in Different Layers of  $\text{KMgF}_3\text{:Eu}$**

$\text{KMgF}_3\text{:Eu}$ (1 mol %)	$I_{197}\%$	$I_{221}\%$	$(I_{197} + I_{221})\%$
top layer	10	21	31
middle layer	6	24	30
bottom layer	9	21	30

The calculated results showed that the oxygen content in the top, middle, and bottom layers was nearly the same. To study the substitution relationships of  $\text{O}^{2-}$  and  $\text{F}^-$ , the crystal was grounded into powder in air. The band emission intensity of 370–700 nm increased sharply (Figure 5), and the maximum value was at 406 and 520 nm. Figure 6 showed the diffuse reflectance spectrum of the  $\text{KMgF}_3\text{:Eu}^{2+}$  powder. Comparing the diffuse reflectance spectrum of the powder with the absorption spectrum (Figure 4), we found that the



**Figure 6.** The diffuse reflectance spectra of  $\text{KMgF}_3\text{:Eu}^{2+}$  crystal grounded into powder at 300 K.

absorption of oxygen at 226 nm increased, but the  $\text{Eu}^{2+}$  absorption decreased greatly and shifted its maximum absorption from 250 and 290 to 340 nm. These results showed that during grinding, the reaction of  $\text{O}^{2-}$  substituting for  $\text{F}^-$  occurred in the damaged crystal interface, which resulted in a large amount of  $\text{Eu}^{2+}\text{O}^{2-}$  centers in the powder. Thus, the emission at 406 nm in the powder came from  $\text{Eu}^{2+}\text{O}^{2-}$  centers. The maximum emission at 520 nm disappeared completely after the crystal and powder was annealed, which suggested that this emission came from the color center. The lift-time of the  $\text{Eu}^{2+}$  fluorescence at 359 nm and the color center at 520 nm was 2.82 and 2.90 ms, respectively, which further confirmed that the fluorescence at 520 nm resulted from the color center.

## Conclusion

In unirradiated  $\text{KMgF}_3$  crystals doped with  $\text{Eu}^{2+}$ , color centers with emission in the range of 400–700 nm existed, the maximum emission was at 420 nm, and the  $\text{Eu}^{2+}$  could transfer energy to these color centers. The annealing experiment confirmed that the 420 nm emission in the crystal resulted from both the color center and the oxygen centers, but the color centers were dominant. With the damage of crystals, the displacement of  $\text{O}^{2-}$  to  $\text{F}^-$  occurred.

**Acknowledgment.** We thank Dr. James R. Kincaid and Dr. S. A. Reid of the chemistry department of Marquette University for providing the setup of high-resolution emission and decay-time measurements. This work was supported by the national key project for fundamental research.

CM010648Q