



Solvothermal fabrication and luminescent properties of $\text{Eu}^{2+}/\text{Gd}^{3+}$ doped potassium magnesium fluoride



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ABSTRACT

Phase-pure Gd-/Eu-doped and co-doped KMgF_3 phosphors are synthesized by solvothermal techniques at 200 °C for 5 days. The crystal structure, particle size and morphologies of the as-synthesized products are investigated by X-ray powder diffraction (XRD) and environment scanning electron microscopy (ESEM). The excitation and emission spectra of the rare earth ions doped KMgF_3 are measured by the fluorescence spectrophotometer and the effects of Gd^{3+} ions molar fraction on the luminescence of Eu^{2+} ions are discussed. In the co-doped Eu^{2+} and Gd^{3+} system, the emission intensity of Eu^{2+} ion gradually increases with the increasing Gd^{3+} concentration, and the enhancement of Eu^{2+} fluorescence is due to an efficient energy transfer from Gd^{3+} to Eu^{2+} in the host. In addition, the mechanism of energy transfer has been discussed in detail. These results suggest that the phosphors of $\text{KMgF}_3: \text{Gd}^{3+}, \text{Eu}^{2+}$ would become promising short-wave laser materials.

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1. Introduction

Perovskite complex fluorides doped with rare-earth-ions are of considerable importance for a wide variety of applications, such as hosts for luminescence centers [1], active media in the most efficient up-conversion luminescent materials [2], laser photo-sources [3], neutron scintillation detectors [4], and so on. Among these complex fluorides, KMgF_3 , with a typical cubic perovskite, has attracted enormous interest recently due to several advantages: better optical homogeneity, low melting, high thermal stability, isotropy, and high optic diaphaneity [5], which has been widely used as host materials for rare earth doped solid state lasers and phosphors. It is well-known that KMgF_3 has great potential adhibitions in thermoluminescent dosimeter and window materials in the ultra-violet (UV) and vacuum-ultra-violet (VUV) wavelength region [6] and is a host of ideal optical function materials for searching for a new solid-state laser [7].

The divalent europium ion is an important low valence rare earth ion. The emission and absorption spectra of Eu^{2+} usually consist of broad bands due to transitions between the $^8\text{S}_{7/2}$ ($4f^7$) ground state and the crystal field components of the $4f^65d$ excited state configuration [8]. Since the involved 5d orbitals are external, the position of these energy levels and consequently the

wavelength of excitation and emission bands strongly depend on the host crystal. The emission spectra of the europium-doped KMgF_3 belong to the sharp line emission located at around 360 nm arising from f–f transition, which is an important research object to explore for short-wave visible solid laser materials. The studies with regard to the spectral properties of the 360 nm emission peak arising from f–f transition of Eu^{2+} in the KMgF_3 host lattice have been more reported at home and abroad [9–12].

Gd^{3+} is a widely used luminescence activator in optical materials and its properties are well known. Under excitation of VUV and UV light, the emission peak of Gd^{3+} appears in the ultraviolet region where a lot of rare earth ions have strong absorption of light energy. It means that the emission peak of Gd^{3+} tends to overlap with the excitation band of many rare earth ions in this region. Therefore, Gd^{3+} is also a good sensitizer in most host matrixes [13]. Many researches on the energy transfer from Gd^{3+} as a matrix ion to other ions with different hosts, such as the energy transfer phenomenon of the $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$ in LiGdF_4 by quantum cutting [14], have been published [15–17]. However, to the best of our knowledge, few reports have been made regarding the luminescence properties and energy transfer of KMgF_3 doped and co-doped with $\text{Gd}^{3+}, \text{Eu}^{2+}$ ions.

Generally, pure and doped complex fluorides crystals can be prepared by conventional high-temperature solid-state reactions [18], Bridgman–Stockbarger method [5], sol–gel [19], mild hydrothermal [20] and solvothermal process [21]. Among the

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various synthesis methods, the solvothermal route is of considerable interest. The solvothermal method, benefiting from a relatively low growth temperature, an approximate thermodynamic equilibrium growth condition, and the formation of phase-pure and –homogeneous materials, is a convenient solution technique for the fabrication of fluorides with the well-structured and the uniform size distribution [22].

In this study, a facile solvothermal method is employed to synthesize phase-pure Gd-/Eu-doped and co-doped KMgF_3 phosphors. The structure, morphologies and luminescent properties of the as-synthesized particles are investigated. Energy transfer mechanism in the co-doped KMgF_3 system is also analyzed in detail. It is hoped to develop a novel feature of the rare-earth luminous or short-wave solid-state laser materials in a single matrix doped with different rare earth ions.

2. Experimental

A series of complex fluorides KMgF_3 doped Eu or/and Gd were prepared by solvothermal method, which was carried out in a 20 mL Teflon-lined stainless steel autoclave under autogenous pressure, using $\text{KF}\cdot 2\text{H}_2\text{O}$ (A. R.), MgF_2 (A. R.), EuF_3 (99.99%) and GdF_3 (99.99%) as raw materials. Here we took the fabrication of $\text{KMgF}_3: 0.02$ Gd (mol fraction) as an example to illustrate the process of synthesis. The molar ratios of initial mixtures were 1.0 $\text{KF}\cdot 2\text{H}_2\text{O}$: 1.0 MgF_2 : 0.02 GdF_3 . The typical synthesis procedure was as follows: 0.9413 g $\text{KF}\cdot 2\text{H}_2\text{O}$ (0.01 mol), 0.6230 g MgF_2 (0.01 mol) and 0.0428 g GdF_3 (0.0002 mol) were mixed and homogenized thoroughly (all the grinding was done with agate pestle and mortar) and added into a Teflon-lined autoclave. Then the autoclave was filled with ethylene glycol up to 80% of the total volume. The autoclave was sealed into a stainless steel tank and heated in an oven at 200 °C for 5 days. After being cooled to room temperature naturally, the final powder products were filtered off, washed with absolute ethanol and distilled water, and then dried in air at ambient temperature. Excess ions were removed during washing. For the synthesis of $\text{KMgF}_3:\text{Eu}$ and $\text{KMgF}_3:\text{Gd}$, Eu, the mole ratios of initial mixtures were 1.0 $\text{KF}\cdot 2\text{H}_2\text{O}$: 1.0 MgF_2 : 0.02 EuF_3 and 1.0 $\text{KF}\cdot 2\text{H}_2\text{O}$: 1.0 MgF_2 : 0.02 GdF_3 : 0.02 EuF_3 . The other operations were the same as the synthesis process of $\text{KMgF}_3: 0.02$ Gd (mol fraction).

All products were characterized by X-ray powder diffraction (XRD), using a Japan Rigaku D/max-IIB diffractometer with $\text{CuK}\alpha_1$ radiation ($\lambda = 0.1541$ nm). The XRD data for index and cell-parameter calculations were collected by a scanning mode with a step of 0.02° in the 2θ range from 10° to 100° and a scanning rate of $4.0^\circ \text{ min}^{-1}$ with silicon used as an internal standard. Particle-size and morphology were performed on a Hitachi S-570 environment scanning electron microscopy (ESEM). Gold was used to coat the particles as a means to reduce charging effects. The luminescence spectra were measured using a Hitachi F-4500 fluorescence spectrometer equipped with a monochromator (resolution: 0.2 nm) and 150 W Xe lamp as the excitation source. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 1a shows the XRD pattern of the as-prepared $\text{KMgF}_3: 0.02$ Eu powder. All the peaks in Fig. 1a can be in good agreement with the standard JCPDS card (No. 18-1033). No other peaks or impurities are detected. Therefore, XRD confirms the sample obtained under mild solvothermal conditions is in a pure cubic phase (space group: $\text{Pm}\bar{3}\text{m}$ [221]) of KMgF_3 . It can also be seen from the XRD patterns of Gd (Fig. 1b) or Eu-Gd (Fig. 1c) co-doped KMgF_3 at the dopant of 0.02 (mol fraction) that the crystal structures are still cubic, which is the same as that of $\text{KMgF}_3: 0.02$

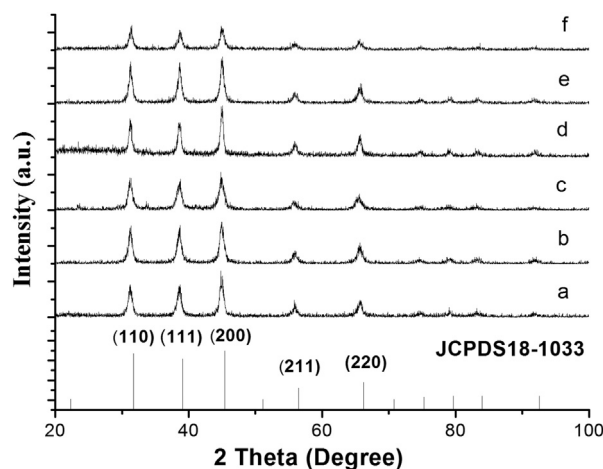


Fig. 1. XRD patterns of (a) $\text{KMgF}_3: 0.02$ Eu; (b) $\text{KMgF}_3: 0.02$ Gd; (c) $\text{KMgF}_3: 0.02$ Eu, x Gd. (c. $x = 0.02$; d. $x = 0.04$; e. $x = 0.06$; f. $x = 0.08$).

Eu (Fig. 1a). The result shows that at the dopant concentration of 0.02 Eu or/and 0.02 Gd the obtained products are free from impurities and the structure can not be changed by a low doping concentration of rare-earth ions.

With the increasing of the concentration of Gd^{3+} ion in the co-doped Eu^{2+} and Gd^{3+} system, the intensity of the diffraction peaks of the crystal plane (110), (111) and (200) gradually enhances as can be seen from Fig. 1, indicating that the crystallinity of the crystal is gradually getting better. When the dopand content of Gd^{3+} ion equals 0.06, the intensity of the diffraction peak is the largest, and the crystallinity of the crystal is the best as seen in Fig. 1d. As the concentration of Gd^{3+} ion continues to increase, the intensity of the diffraction peaks gradually decreases as shown in Fig. 1e and 1f due to the distortion of the lattice structure and the deterioration of the crystallinity of the crystal. The lattice constants of the samples are shown in Table 1 through calculation. From Table 1, as the concentration of Gd^{3+} ion increases, the volume of the unit cell gradually decreases, this is because Gd^{3+} or Eu^{2+} gradually replaced the K^+ sites as plotted in Fig. 2, and the ionic radius of Eu^{2+} (0.112 nm) and Gd^{3+} (0.0938 nm) are smaller than those of K^+ (0.133 nm) in the co-doped system.

The morphology of the samples is examined by ESEM at room temperature. Fig. 3 shows the environment scanning electron micrograph (ESEM) images of the rare-earth ion-doped KMgF_3 . As can be seen from these figures, the powders are cubic with good shape, indicating that the products are pure phase. Uniform grain texture of KMgF_3 doped with rare-earth ions can be observed with grain sizes about 153 nm, 167 nm and 320 nm, respectively.

Fig. 4 portrays the photoluminescence excitation and emission spectra of Gd^{3+} or Eu^{2+} singly-doped phosphors and Gd^{3+} - Eu^{2+} co-doped phosphors at the room temperature. The excitation spectrum of $\text{KMgF}_3: 0.02$ Gd^{3+} phosphors monitored at 313 nm, is shown on the left-hand side of Fig. 4a. The excitation peak is located at 275 nm, which corresponds to the electronic transitions from the $4f$ ($^8\text{S}_{7/2}$) ground state to the $^6\text{I}_{7/2}$ excited state of Gd^{3+} .

Table 1
Calculated lattice constants of $\text{KMgF}_3: 0.02$ Eu, x Gd samples.

x	a/nm	v/nm ³
0.00	0.40647	0.06715
0.02	0.40112	0.06454
0.04	0.40406	0.06597
0.06	0.40135	0.06465
0.08	0.40095	0.06446

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