Optics & Laser Technology 81 (2016) 162–167

Contents lists available at ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Full length article

Hydrothermal synthesis and spectral properties of Ce^{3+} and Eu^{2+} ions doped $KMgF_3$ phosphor

Guoxian Zhu [a,b], Mubiao Xie [a,*], Qu Yang [b], Yingliang Liu [b,**]

[a] School of Chemistry and Chemical Engineering, Institute of Physical Chemistry, Lingnan Normal University, Zhanjiang 524048, PR China
[b] Department of Chemistry and Institute of Nanochemistry, Jinan University, Guangzhou 510632, PR China

ARTICLE INFO

Article history:
Received 2 August 2015
Accepted 23 September 2015
Available online 17 February 2016

Keywords:
$KMgF_3$
Rare earth
Optical properties
Hydrothermal synthesis

ABSTRACT

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

1. Introduction

The application of complex metal fluorides as active media in the most efficient up-conversion luminescent materials [1], laser photosources [2] and neutron scintillation detectors [3] is well established. Among these complex fluorides, the best example is $KMgF_3$ because of several advantages: better optical homogeneity, low melting, high thermal stability, isotropy, and high optic diaphaneity. It is considered that $KMgF_3$, with a typical cubic perovskite, is a host of ideal optical function materials for searching for a new solid-state laser [4] and has great potential adhibitions in thermoluminescent dosimeter and window materials in the ultra-violet (UV) and vacuum-ultra-violet (VUV) wavelength region [5]. It is well known that pure and doped complex fluorides crystals can be prepared by conventional high-temperature solid-state reactions [6], Bridgman–Stockbarger method [7] and high temperature (> 400 °C), high-pressure (> 100 MPa) hydrothermal technique [8], Sol–Gel [9], mild hydrothermal and solvothermal process [10–12]. Among the various synthesis methods, the hydrothermal route is of considerable interest. The hydrothermal method, benefiting from a relatively low growth temperature and an approximate thermodynamic equilibrium growth condition, can fabricate the formation of phase-pure and -homogeneous materials crystals with the well-structured, the uniform size distribution and high crystallinity [13].

In this paper, phase-pure Ce-/Eu-doped and co-doped $KMgF_3$ phosphors are prepared by a facile hydrothermal method and their luminescent properties of the as-synthesized particles are investigated. Energy transfer mechanism in the co-doped $KMgF_3$ system is also analyzed. It is hoped to develop a novel feature of the rare-earth luminous or 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 Ce were prepared by hydrothermal method, which was carried out in a 20 mL Teflon-lined stainless steel autoclave under autogenous pressure, using K_2CO_3 (A.R.), $MgCO_3$ (A.R.), NH_4HF_2 (A.R.), EuF_3 (99.99%) and CeF_3 (99.99%) as raw materials. Here we took the fabrication of $KMgF_3$: 0.02 Ce (mol fraction) as an example to illustrate the process of synthesis. The molar ratios of initial mixtures were 1.0 K_2CO_3: 1.0 $MgCO_3$: 0.02 CeF_3. The typical synthesis procedure was as follows: 0.1382 g K_2CO_3 (0.01 mol), 0.0843 g $MgCO_3$ (0.01 mol) and 0.0394 g CeF_3 (0.0002 mol) were mixed and homogenized thoroughly (all the grinding was done with agate pestle and mortar) and the de-ionized water was added into the mixture with slow heating and stirring. After dissolved, the

---

[*] Corresponding author. Fax: +86 0759 3183510.
[**] Corresponding author. Fax: +86 20 85221697.
E-mail address: tliuyl@163.com (M. Xie).

http://dx.doi.org/10.1016/j.optlastec.2015.09.027
0030-3992/© 2016 Published by Elsevier Ltd.

mixture was quickly transferred into a Teflon-lined stainless-steel autoclave of 20 mL capacity. Then 2.8525 g NH_4HF_2 (0.05 mol) was carefully added into the autoclave under stirring. The autoclave was filled with appropriate de-ionized water up to 70–75% of the total volume. Subsequently hydrofluoric acid (40 mass%, A.R.) was used to adjust the pH to 4–5. The autoclave was sealed into a stainless-steel tank and heated in an oven at 200 °C under autogenous pressure for 5 days. After being cooled to room temperature naturally, the resultant precipitate was centrifuged and washed with distilled water several times to pH ca. 7, and then dried in air at ambient temperature. Excess ions were removed during washing. For the synthesis of $KMgF_3$: Eu and $KMgF_3$: Ce, Eu, the mole ratios of initial mixtures were 1.0 K_2CO_3: 1.0 $MgCO_3$: 0.02 EuF_3 and 1.0 K_2CO_3: 1.0 $MgCO_3$: 0.02 CeF_3: 0.02 EuF_3. The other operations were the same as the synthesis process of $KMgF_3$: 0.02 Ce (mol fraction).

All products were characterized by X-ray powder diffraction (XRD), using a Japan Rigaku D/max-IIB diffractometer with Cu$K\alpha_1$ radiation (λ=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 $°min^{-1}$ 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. X-ray photoelectron spectra (XPS) were recorded on a VG Scientific MAR-II X-ray photoelectron spectroscopy, using non-monochromated MgKα radiation as the excitation source. Binding energy values (Eb) were all referenced to carbon 1s line taken as 285.00 eV. Detecting vacuum was 1.33×10^1 Pa. 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

3.1. Description of the structure

Fig. 1shows the XRD pattern of the as-prepared $KMgF_3$: 0.02 Ce, 0.02 Eu powder. All the peaks in Fig. 1 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 hydrothermal conditions is in a pure cubic phase (space group: Pm3m [221]) of $KMgF_3$. It can also be seen from the XRD patterns of Eu or Ce-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 $KMgF_3$: 0.02 Ce, 0.02 Eu. The result shows that at the dopant concentration of 0.02 Eu or/and 0.02 Ce the obtained products are free from impurities and the structure can not be changed by a low doping concentration of rare-earth ions.

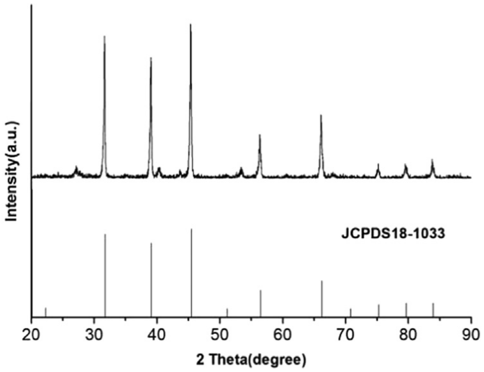

Fig. 1. XRD pattern of $KMgF_3$: 0.02 Ce, 0.02 Eu.

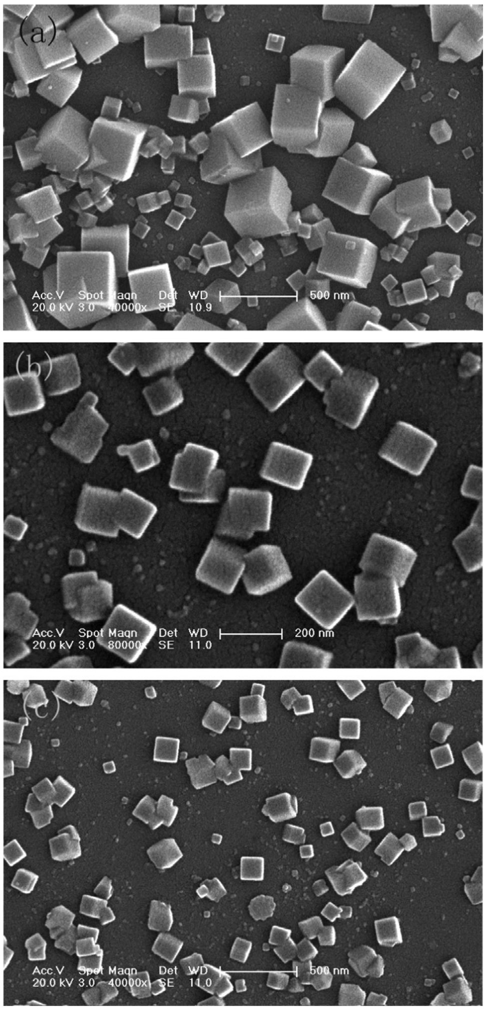

Fig. 2. ESEM images of $KMgF_3$: Eu^{2+} (a), $KMgF_3$: Ce^{3+} (b) and $KMgF_3$: Eu^{2+}, Ce^{3+} (c).

3.2. Shape and size

The morphology of the samples is examined by ESEM at room temperature. Fig. 2 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, which can be obtained via a crystallization–dissolution–recrystallization–self-assembly growth process [14]. Under mild hydrothermal synthesis, the reactant ions can move freely in the solution and make contact with each other directionally and completely, indicating that the pure phase can be fabricated. Uniform grain texture of $KMgF_3$ doped with rare-earth ions can be observed with grain sizes about 2.5 μm, 130 nm and 2.2 μm, respectively.

3.3. X-ray photoelectron spectra (XPS) of $KMgF_3$: Eu^{2+}

It is well known that the content of oxygen in complex fluorides synthesized by hydrothermal method is lower than that of the corresponding complex fluorides synthesized by high temperature solid-state reaction [13,15]. In the hydrothermal synthesis system, OH^- is present. Because the OH^- ionic radius is similar to that of F^- ion, complex fluorides containing oxygen may be obtained.