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Synthesis and fluorescence properties of cerium–$KMgF_3$ through a solvothermal process

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Abstract

Phosphor of $KMgF_3$:Ce^{3+} is synthesized through solvothermal method at 180 °C and characterized by means of X-ray powder diffraction (XRD) and environment scanning electron microscopy (ESEM). X-ray photoelectron spectroscopy (XPS) is applied to the study of the energy band structure of $KMgF_3$:Ce^{3+} and confirms the oxygen content of the product is very low. The fluorescence spectra of the rare-earth ion-doped $KMgF_3$ is investigated by the fluorescence spectrophotometer. In the emission spectra, there is a broadband emission with a maximum center located at 306 nm arising from d-f transition of Ce^{3+} in the host. This will be useful for ultraviolet tunable lasers.

Keywords: Solvothermal synthesis; Ce^{3+} ions; $KMgF_3$; Luminescence; X-ray photoelectron spectroscopy (XPS)

Rare-earth ion-doped fluorides have been investigated for several decades due to their electrical and optical properties and wide applications as solid electrolytes, green up-conversion phosphors, and optical amplifiers [1–3]. Among these complex fluorides, $KMgF_3$ is specially important because of several advantages: better optical homogeneity, high thermal stability, low melting, 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].

The lowest energy state of Ce^{3+} in crystals has a single 4f electron outside the closed shells. The state is split into $^2F_{5/2}$ and $^2F_{7/2}$ with separation energy of 2250 cm^{-1} by spin–orbit interaction. The next highest state with 30,000–60,000 cm^{-1} in energy has a 5d electron. It generally presents the d-f transition that the electric dipole allows and takes on the form of band emission. The spatially diffuse 5d electron orbital extends outward from the ion to overlap the neighbouring ligand ions, and is more strongly influenced by their motion. In consequence, the optical properties depend strongly on structure of host crystals [5]. Therefore, it can give out light from purple to red and has broader energy distribution. The d-f transition of Ce^{3+} has been intensively studied in the fluorides or complex fluorides [6–9].

Ce^{3+}-doped $KMgF_3$ has attracted interest for its possible application as scintillator [10], as short-wave state laser[11] and as sensitive dosimeter [12,13]. When phosphors are prepared by conventional solid-state route by

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heating in air, usually unwanted impurities like OH^-, O^{2-}, etc., get incorporated [14]. Such impurities can be quite detrimental to the luminescence processes. Especially, fluorides are highly susceptible to the oxygenic content. To get over this difficulty, phosphors are prepared through a solvothermal process [15] which requires a simple set-up and is a convenient method. These results provide an experimental pathway by which phosphors of the lower oxygenic content and tunable solid-state lasers can be realized.

1. Experimental

Solvothermal synthesis of $KMgF_3$ powder is carried out in a 20 mL Teflon-lined stainless steel autoclave under autogenous pressure. The starting reactants are $KF{\cdot}2H_2O$ (A.R.) and MgF_2 (A.R.). The molar ratios of initial mixtures are 1.0 $KF{\cdot}2H_2O$:1.0 MgF_2. The typical synthesis procedure is as follows: 0.9413 g $KF{\cdot}2H_2O$(0.01 mol), 0.6230 g MgF_2(0.01 mol) are mixed and added into a Teflon-lined autoclave. Then the autoclave is filled with ethylene glycol up to 80% of the total volume. The autoclave is sealed into a stainless steel tank and heated in an oven at 180 °C for 7 days. After being cooled to room temperature naturally, the final powder products are filtered off, washed with absolute ethanol and distilled water, and then dried in air at ambient temperature. For the synthesis of $KMgF_3$:Ce^{3+}, the mole ratios of initial mixtures are 1.0 $KF{\cdot}2H_2O$:1.0 MgF_2:0.02CeF_3. The other operations are the same as the synthesis process of $KMgF_3$.

All products are characterized by X-ray powder diffraction (XRD), using a Japan Rigaku D/max-IIB diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 0.1541$ nm). Observation of crystallites by ESEM is performed on a Hitachi S-570 environment scanning electron microscopy. X-ray photoelectron spectra (XPS) are recorded on a VG Scientific MAR-II X-ray photoelectron spectroscopy. Luminescence spectra are measured using a Hitachi F-4500 fluorescence spectrometer. All measurements are carried out at room temperature.

2. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared $KMgF_3$ 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, X-ray diffraction confirms the sample obtained under mild solvothermal conditions is a pure cubic phase (space group: Pm3m [221]) of $KMgF_3$. It can also be seen from the XRD patterns of Ce-doped $KMgF_3$ at the dopant of 0.02 (mol fraction) that the crystal structures of Ce-doped $KMgF_3$ are still cubic lattice, which is the same as that of $KMgF_3$.

The morphology of the samples is examined by ESEM at room temperature. Fig. 2 shows the environment scanning electron micrograph of $KMgF_3$:0.02 Ce^{3+}. As can be seen from this photo, the powder is cubic with good shape, indicating that the product is a pure phase. Uniform grain texture of $KMgF_3$ can be observed with grain sizes about 5.1 μm.

It is well known that the oxygen content of those complex fluorides, which were prepared by solid-state reaction at high temperature, is very high, although the reactions were processed under inert gas protection [16]. In the solvothermal synthesis system, OH^-, which is coming from a trace of water in the solvent, is present. Because the

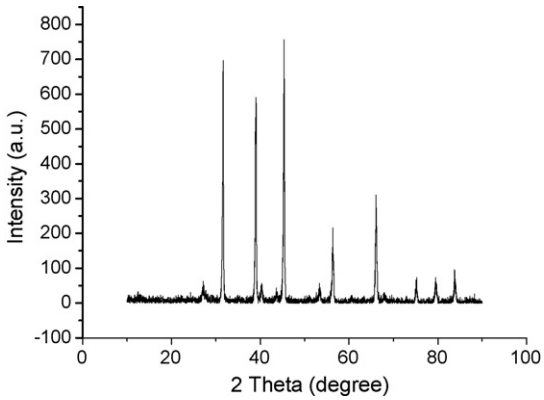

Fig. 1. XRD pattern of $KMgF_3$ powder.