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Enhanced luminescence of $Ca_2MgSi_2O_7:Eu^{2+}$ fibers by sol–gel assisted electrospinning

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ABSTRACT

$Ca_2MgSi_2O_7:Eu^{2+}$ fibers were successfully fabricated by a sol–gel assisted electrospinning and subsequently calcination procedure. The phase formation, morphology and the luminescent properties of the fibers were determined. Two strong Eu^{2+} emission centers were observed in the emission spectrum, which were ascribed to two types of cation sites existing in the $Ca_2MgSi_2O_7$ lattice, respectively. The $Ca_2MgSi_2O_7:Eu^{2+}$ fibers reveal bright green-emitting under the excitation of near UV and blue lights. Compared with the powder sample, the luminescent fibers had average grain sizes less than 1 μm and could be synthesized at a relatively lower temperature. The green luminescence in the luminescent fibers was also greatly enhanced. The intensity of the major peak at 539 nm was stronger and had longer average decay time than that at 466 nm. The $Ca_2MgSi_2O_7:Eu^{2+}$ fibers are expected to be used for optical detectors, bio-labeling and full-color display devices.

1. Introduction

The emission from 5d to 4f of Eu^{2+} is highly efficient and its emission wavelength is strongly dependent on the host lattice so that different color from blue to red can be obtained [1–3]. $Ca_2MgSi_2O_7:Eu^{2+}$ phosphors have been widely investigated due to its efficient green luminescence and high chemical stability [4,5]. However, almost all the reported $Ca_2MgSi_2O_7:Eu^{2+}$ were synthesized by solid-state reaction above 1300 °C. In addition, the grain sizes more than 10 μm and the impurity phases in the product were usually observed by the solid-state route, both of which could greatly reduce the luminescent brightness of the product [6].

The $Ca_2MgSi_2O_7:Eu^{2+}$ fibers are expected to be used for optical devices because of their geometry advantage and high luminescence efficiency. Compared to $Ca_2MgSi_2O_7:Eu^{2+}$ powders, $Ca_2MgSi_2O_7:Eu^{2+}$ fibers provide a better model system to investigate the dependence of electronic transport and optical properties on size confinement and dimensionality [7]. Recently, researches on rare-earth ion doped luminescent fibers have drawn a great deal of attention. Yu et al. [8] synthesized Eu-doped yttria fibers and reported their luminescent properties. The one-dimensional shape results in obvious improvements color purity and relative luminescence intensity [9]. Electro-spinning is a convenient and widely used method for fabricating polymeric and inorganic nano-fibers since first reported by Formhals et al. [10,11]. In a typical process for preparing electrospun inorganic fibers, a sol–gel precursor solution with polymeric binders is first extruded from the orifice of a needle under a high electrostatic field and the polymeric binders are then removed during the subsequent calcination of the fibrous precursor [12].

In this study, silicate sol–gel precursors mixed with 10 wt.% Polyvinyl Alcohol (PVA) were electrospun into fibers and the $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers were prepared after subsequent calcination. Enhanced luminescence of Eu^{2+} in $Ca_2MgSi_2O_7$ fibers is achieved. Several possible mechanisms for the enhanced luminescent efficiency are discussed.

2. Experiments

In this study, analytical grade $Ca(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Si(OC_2H_5)_4$ (TEOS), $Eu(NO_3)_3{\cdot}6H_2O$ were used to prepare precursor. Firstly, certain amounts of $Ca(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $Eu(NO_3)_3{\cdot}6H_2O$ were dissolved in DI water; the solution was mixed at 50 °C for 30 min. Secondly, TEOS and ethanol were added to the solution and the pH value of the mixed solution was controlled at 4.0. Finally, the solution was stirred for 1 h to obtain transparent solution and a certain amount of PVA (MW = 300,000) aqueous solution (10 wt.%) was added to obtain a homogeneous hybrid sol for electrospinning.

The spinnable sol was loaded in a plastic syringe. The distance between the spinneret (a metallic needle) and collector (a piece of flat aluminum foil) was fixed at 17 cm, and the high-voltage

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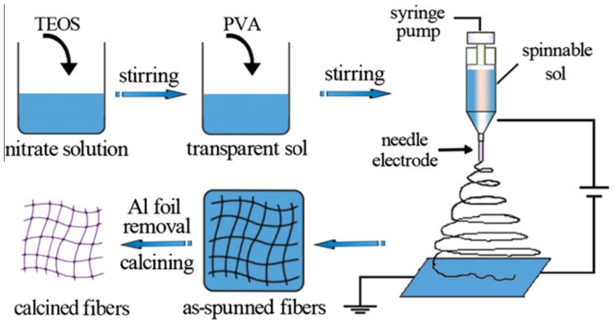

Fig. 1. Schematic diagram of the preparation of the $Ca_2MgSi_2O_7:Eu^{2+}$ fibers.

supply was maintained at 13 kV. The spinning rate was controlled at 0.5 ml/h. To obtain $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers, the as-spinned hybrid fibers were calcined at 1150 °C for 4 h in a carbon monoxide reducing atmosphere. The schematic of the preparation of the $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fiber was shown in Fig. 1.

For comparison, the $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ powders were synthesized. Analytical grade $Ca(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$ and SiO_2 powders were weighed, mixed and milled thoroughly in an agate mortar for 2 h according to the nominal compositions of the $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$. The mixture was calcined at 1300 °C for 7 h in the carbon monoxide reducing atmosphere.

XRD data were collected on a Rigaku D/Mx diffractometer operating at 40 kV, 30 mA with Bragg–Brentano geometry using Cu Kα radiation (λ = 1.5405 Å). The morphologies of the samples were observed by scanning electron microscopy (FE-SEM, S-4700, Hitachi, Japan) equipped with energy dispersive spectroscopy (EDS). The excitation and emission spectra were recorded on a Perkin–Elmer LS-50B luminescence spectrometer with Monk–Gillieson type monochromators and a 150 W Xenon discharge lamp as excitation source.

3. Results and discussion

3.1. Phase composition and morphology

Fig. 2 shows the XRD patterns of the $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers and the powder sample. The diffraction peaks can be indexed to a pure tetragonal structured $Ca_2MgSi_2O_7$ (JCPDs card no. 35-0592, a = 7.8332 Å, and c = 5.0096 Å) with lattice constants of a = 7.8370 Å, and c = 5.008 Å for the fibers, and a = 7.8350 Å, c = 5.009 Å for the powder sample, respectively. No impurity peaks were detected in the scanning range, which indicates that the Eu^{2+} was completely incorporated into the $Ca_2MgSi_2O_7$ lattice according to the crystal structure of $Ca_2MgSi_2O_7$, reported by Ling Jiang et al. [13]. The possible sites for incorporating Eu^{2+} (1.12 Å) in the $Ca_2MgSi_2O_7$ lattice are Ca^{2+} (1.12 Å) sites, Mg^{2+} (0.65 Å) sites, or Si^{4+} (0.41 Å) sites. Because Ca^{2+} is similar in size as Eu^{2+}, it is more likely that Eu^{2+} prefers to enter an $[CaO_8]$ site rather than the tetrahedral $[MgO_4]$ and $[SiO_4]$ sites. In comparison with the unit cell volume of $Ca_2MgSi_2O_7$ (307.22 Å^3), the unit cell volumes of $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers and powder sample were 307.58 Å^3 and 307.50 Å^3, respectively. The results indicate that the incorporation of Eu^{2+} ions into the $Ca_2MgSi_2O_7$ crystal lattice does not cause any significant lattice distortions.

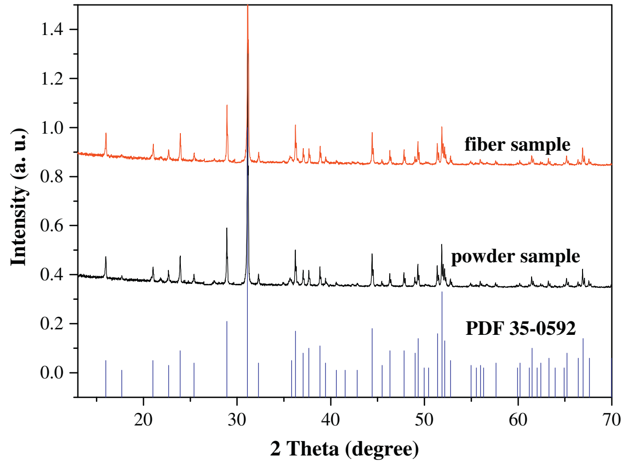

Fig. 2. XRD patterns of $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers, powder sample and JCPDs card no. 35-0592.

Fig. 3 shows SEM images of as-spinned fibers (a), $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers calcination at 1150 °C for 4 h, with a magnified image in the inset (b), and the image of powder sample (c) synthesized by calcination at 1300 °C for 7 h. The results in Fig. 3a showed that the as-spun hybrid fibers are smooth and uniform with a diameter range from 0.6 to 0.9 μm. After calcined at 1150 °C, the original integrity of as-spun fibers was retained after the decomposition of PVA binder, and no shrinkage in fiber diameter was detected (Fig. 3b). $Ca_2MgSi_2O_7:Eu^{2+}$ fibers had many fine and closely linked submicron-particles on the surface, which orderly arranged along the axis of the fiber. The variation in the diameter along the axes of the fibers is small and the average diameters of fibers ranged from 0.6 to 0.9 μm. Moreover, after further calcination and grain growth, the so-called "bamboo wires" appeared and the pores disappeared, which may be attributed to thermal grooving [14]. Due to the increased calcining temperature, atomic diffusion became more active in the fiber, allowing for the redistribution of atoms from high chemical potential status to low chemical potential status, eliminating rough surface to lower the interfacial energy, as shown in the inset of Fig. 3b. EDS analyses of the electrospun fibers calcined at 1150 °C revealed the presences of O, Si, Mg, Ca and Eu, agreeing with the elemental composition of $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ (Fig. 3d). The powder sample had a particle size range from 3 to7 μm and some rigid aggregates also appeared (Fig. 3c), indicating broad size distribution and decreased surface/volume ratio of particles.

3.2. Photoluminescence properties of $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers

In order to investigate the luminescent properties of the fibers, PL measurement was carried out and Figs. 4 and 5 are emission and excitation spectra of the $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers, respectively. Upon excitation in the UV region, the emission spectra consist of two broad emission bands, with emission maximums at 466 nm and 539 nm. The emission originates from the energy transition between the $4f^7$ ground state and the $4f^65d$ excited state of the Eu^{2+} ions. The emission wavelength of the fibers is slightly longer than that of the powder samples by state solid synthesis (emission maximums at the 465 nm and 536 nm). Compared to the Eu^{2+}-doped powder sample, the emission spectra of the fiber sample show a slight red-shift. This red-shift indicates that the strength of crystal field in the fibers may be a little bit stronger than that in the powder samples. Fig. 4 also shows that there were two Eu^{2+} luminescence centers in $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers. This can be clearly demonstrated by the decomposition of the emission spectrum into two Gaussian components peaked at 469 nm and 538 nm, respectively.

Fig. 5 is the excitation spectra of the $Ca_{1.94}MgSi_2O_7:0.06Eu^{2+}$ fibers. The excitation spectrum acquired at 531 nm consists of a broad absorption band extending from 250 nm to 500 nm with a center at 407 nm. The broad excitation band implies that the