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Low-temperature synthesis and photoluminescence of IIA-VIB nano-phosphors doped with rare earth ions

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Abstract

Eu^{2+} doped CaS nanoparticles were prepared by two kinds of methods, alkoxide and co-precipitation. The as-prepared samples did not show any emission, while the heated samples showed the red emission corresponding to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. No signal of Eu^{2+} was observed in the electron paramagnetic resonance spectra of the as-prepared samples, while the heated samples showed two sets of sextet hyperfine lines corresponding to two isotopes of Eu^{2+} with the mass numbers of 151 and 153. Accordingly, these results indicate that Eu^{2+} ions were incorporated into CaS during subsequent heating to show the red emission.

Keywords: Phosphors; Nanofabrications; Luminescence; Electron paramagnetic resonance

1. Introduction

IIB-VIB doped semiconductor nanocrystals, such as the Mn^{2+}-doped ZnS nano-phosphor can be prepared by wet chemical processes. The surface modification induces the passivation of surface defects and the quantum confinement effect to increase the luminescent efficiency. On the other hand, the preparation of IIA-VIB sulfide phosphors in a solution has been hardly investigated, because IIA-VIB sulfides such as CaS easily react with water to form hydrates. $CaS:Eu^{2+}$ is one of the candidates of optical converter from blue light to red light. A few of works have been reported on the preparation of CaS nanoparticles with and without dopants, such as co-precipitation for $CaS:Eu^{2+}$ [1], alkoxide method for CaS [2] and solvothermal method for CaS, $CaS:Bi^{3+}$, $CaS:Ag^{+}$ and $CaS:Pb^{2+}$ [3,4]. Here we report the wet chemical methods of alkoxide and co-precipitation, followed by heating at low temperature, to synthesize the $CaS:Eu^{2+}$ nano-phosphors. The incorporated paramagnetic centers are characterized by electron paramagnetic resonance (EPR) spectroscopy to understand the relation between EPR results and the photoluminescent properties.

2. Experimental

A non-aqueous solvent was used for preventing the hydrolysis of CaS. (i) *Alkoxide method*: The 150 mL of ethanol (99%, Shinwa Alcohol) in a reactor was bubbled by 300 mL/min N_2 gas with stirring for 30 min to remove the dissolved oxygen. The 96 mmol of $Ca(OC_2H_5)_2$ (99.00%, Soekawa Rikagaku) was suspended in this ethanol, followed by insufflating 50 mL/min H_2S gas to obtain the clear solution. The 50 mL of 38.4 mM $Eu(NO_3)_3$ (99.95%, Kanto Kagaku) ethanolic solution was added to this clear solution. Further insufflating of H_2S gas produced the well-dispersed colloidal solution. (ii) *Co-precipitation method*: The 4 mmol Na_2S (99%, Soekawa Rikagaku) and 0.4 mL 1-thioglycerol (95.00%, Kanto Kagaku) were dissolved in 360 mL ethanol. The 300 mL/min N_2 gas was insufflated into this solution. Then, 80 mL ethanol solution containing 3.96 mmol $CaCl_2$ (99.90%, Soekawa Rikagaku) and 0.04 mmol $EuCl_2$ (99.99%, Aldrich) was put into the sulfide

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solution with vigorous stirring. After 2 h, the precipitate was obtained by adding 100 mL tetrahydrofuran (THF) (99.5%, Kanto Kagaku). The samples prepared by alkoxide and co-precipitation methods denote AL and CO, respectively.

The as-prepared samples, AL and CO, were collected by centrifugation, and dried at 50 °C for 1 day. The dried particles were heated to 700 °C at a rate of 10 °C/min in N_2 gas, kept at the same temperature for 2 h and cooled down to room temperature gradually. Bulk sample was prepared by heating the mixture of CaS and $EuCl_2$ at 1100 °C for 3 h under reducing atmosphere.

The crystal structure was identified by X-ray powder diffractometry (XRD, Rigaku, Rint-2200). The samples were observed by field emission transmission electron microscopy (FE-TEM, Philips, TECNAI F20) at 200 kV. The particle size distribution of the colloidal solution was measured by dynamic light scattering (DLS) method (Malvern, HPPS). Emission and excitation spectra were measured by spectrometer (JASCO, FP6500). EPR spectra were measured by a spectrometer (JEOL, JES-RE3X).

3. Results and discussion

3.1. Particle size distribution and identification of crystalline phase

The colloidal solution of the sample AL keeps well dispersed, while the sedimentation occurs immediately for the sample CO. According to DLS measurement of the former, the average particle diameter is 22 nm, as shown in Fig. 1. The TEM micrograph of the as-prepared sample AL indicates that the diameter of primary particles is about 20–30 nm, as shown in Fig. 2(a). Hence, the agreement between both results of DLS and TEM suggests that the primary particles are well dispersed without agglomeration for the colloidal solution prepared by alkoxide method. Heat treatment induces the coalescence of particles for the samples AL, as shown in Fig. 2(b). In contrast, the aggregation of nanosize particles including less than 20 nm in diameter and their wide size distribution are observed for the as-prepared sample CO (Fig. 2(c)). The morphology and size of the sample CO do not appreciably change after heating, as shown in Fig. 2(d). According to XRD profiles, the as-prepared samples AL and CO are single phase CaS with cubic structure. The heated samples AL and CO contain a small amount of $CaSO_4$.

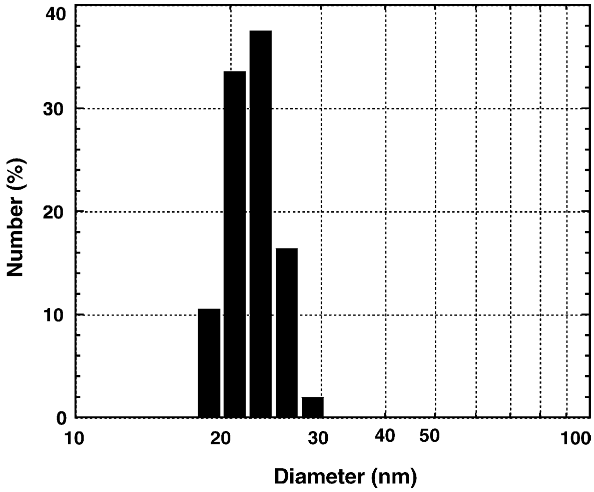

Fig. 1. Particle size distribution of the colloidal solution prepared by alkoxide method.

3.2. Photoluminescent properties

The as-prepared samples AL and CO did not show any emission, while both heated samples showed the red emission corresponding to the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+}, as shown in Fig. 3. The peak wavelength, 627 nm, for the sample AL is close to 628 nm for the sample CO, while these are shorter than 633 nm for bulk. This slight blue-shift by comparison with bulk could be explained by the decrease in the crystal-field strength by nanosizing.

Fig. 4(a) and (b) shows the excitation spectra of the heated samples AL and CO, respectively. The excitation peaks corresponding to the interband transition of CaS are observed at 268 nm for the sample AL and at 254 nm for the sample CO. These wavelengths are smaller than 273 nm for bulk (Fig. 4(c)). This blue-shift suggests the increasing in the band gap, i.e., the quantum size effect. All the samples exhibit the broad peak, ranging from 400 to 600 nm, due to the $4f^7 \rightarrow 4f^6 5d^1$ transition of Eu^{2+}. Several sharp peaks corresponding to the f–f transition of Eu^{3+} are also observed at the region between 460 and 500 nm. The intensity of the peak due to the interband transition relative to that of the $4f^7 \rightarrow 4f^6 5d^1$ transition of Eu^{2+} for the sample CO is three times higher than that of the bulk. This suggests that the increase in the probability of interband transition by quantum size effect. The reason why such an effect is much larger for the sample CO than for the sample AL might be attributed to the effect by surface modification with 1-thioglycerol.

3.3. Observation of paramagnetic species by EPR

The electronic ground states corresponding to the possible valence numbers of +2 and +3 for europium are $^8S_{7/2}$ and $^7F_0$, respectively. Moreover, as the orbital moment is zero for Eu^{2+}, its relaxation time is relatively long. Accordingly, EPR can detect Eu^{2+} at room temperature, but not Eu^{3+}. Consequently, the EPR spectrum of Eu^{2+} incorporated into CaS exhibits two sets of sextet hyperfine lines corresponding to two isotopes of Eu^{2+} (nuclear spin $I = 5/2$) with mass numbers of 151 and 153.

No signal of Eu^{2+} is observed in the EPR spectra of the as-prepared samples AL and CO, while the heated samples show the above-mentioned two sets of hyperfine lines, as shown in Fig. 5. This result indicates that Eu^{2+} ions are incorporated into CaS by heating to show the red emission.

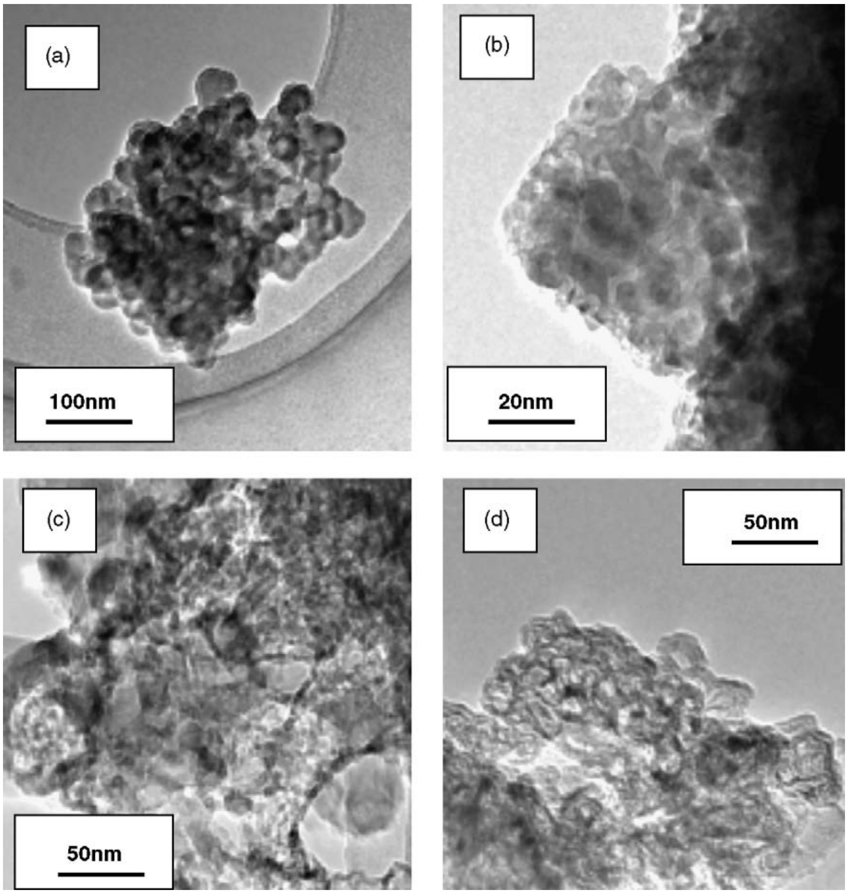

Fig. 2. TEM images of the samples prepared by alkoxide method: (a) as-prepared, (b) heated; by co-precipitation method: (c) as-prepared, (d) heated.

The singlet line of F^+ center, i.e., one electron trapped in a sulfur vacancy is observed in the as-prepared sample CO. In contrast, no F^+ center is observed in the as-prepared sample AL. For the latter, excess sulfur provided by H_2S gas could prevent the formation of F^+ center.

The sextet hyperfine lines corresponding to Mn^{2+} impurity ions [5] is also observed in the as-prepared and heated samples AL, although they are not intentionally doped to CaS. In contrast, the EPR signal of Mn^{2+} is observed only for the heated sample CO. These results suggest that in alkoxide

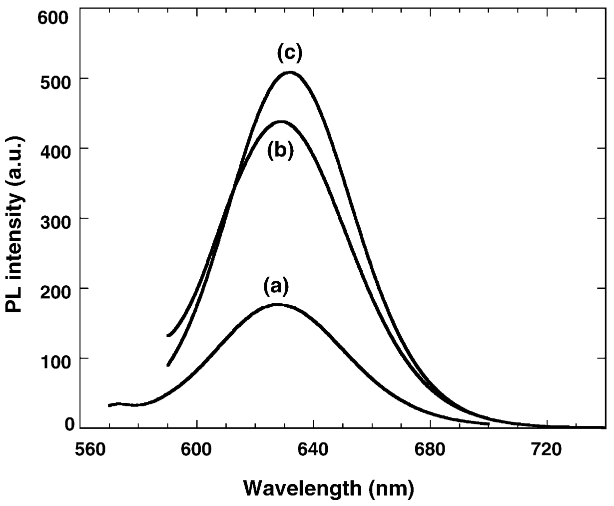

Fig. 3. Emission spectra of the heated samples excited by the $4f^7 \rightarrow 4f^65d^1$ transition: (a) alkoxide method, (b) co-precipitation method, (c) bulk.

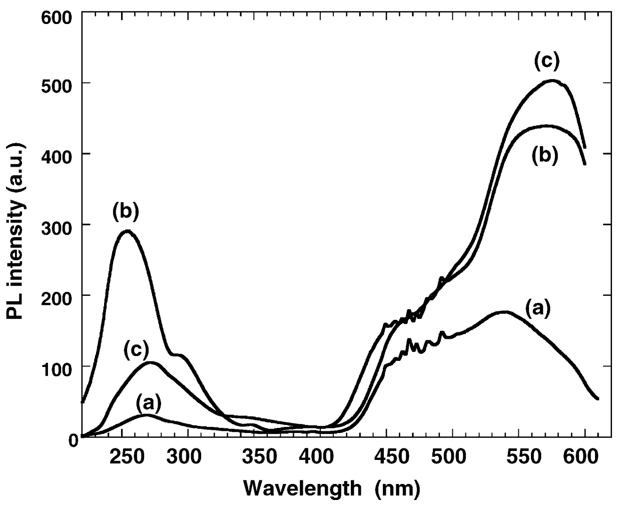

Fig. 4. Excitation spectra of the heated samples: (a) alkoxide method, (b) co-precipitation method, (c) bulk.

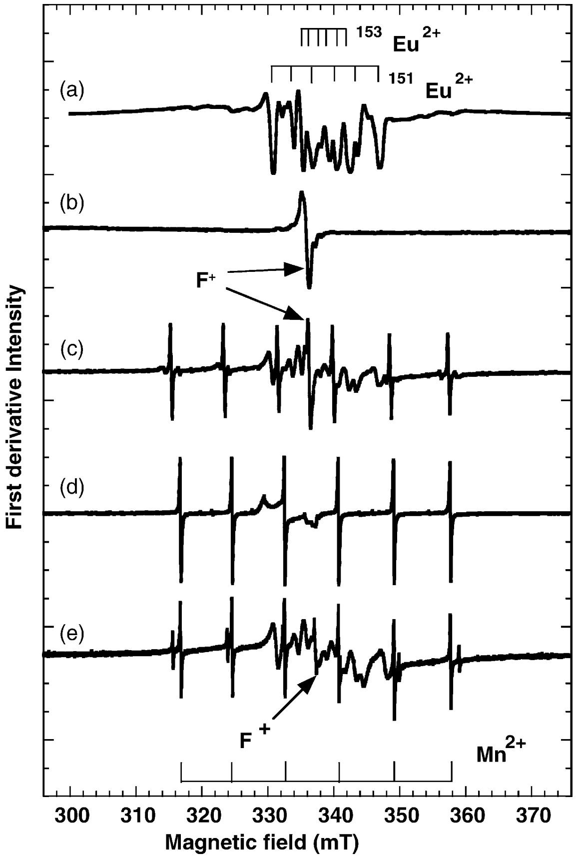

Fig. 5. EPR spectra: (a) bulk, (b and c) co-precipitation method, (d and e) alkoxide method, (b and d) as-prepared, (c and e) heated.

method, it is possible to incorporate dopant ions into CaS without post heat treatment. In this work, the emission due to the d–d transition of Mn^{2+} by exciting the interband of CaS [6] is not clearly observed because of the small Mn content. For the heated sample AL, two sets of sextet hyperfine lines due to Mn^{2+} ions are observed in the EPR spectrum. The hyperfine coupling constant, $|A|$, are 8.19 and 9.19 mT, which correspond to Mn^{2+} incorporated into CaS and $CaSO_4$, respectively. This is consistent with XRD results.

4. Concluding remarks

CaS:Eu^{2+} nanoparticles were prepared by two wet chemical procedures: (i) alkoxide method, (ii) co-precipitation method. Both as-prepared samples does not show any emission, while heating at 700 °C in N_2 incorporates Eu^{2+} into CaS to show the red emission corresponding to the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Quantum size effect is confirmed by the increase in the probability of interband transition of CaS as well as the blue-shift of excitation peak due to its transition. The incorporation of paramagnetic centers of Eu^{2+} and Mn^{2+} into CaS is conformed by EPR spectroscopy. We expect that alkoxide method can be applied for the incorporation of appropriate luminescent centers into sulfide nano-phosphors without post heat treatment.

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