Journal of Alloys and Compounds 488 (2009) 538–540

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Crystal growth of nanoscaled europium selenide having characteristic crystal shapes

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ARTICLE INFO

Article history:
Received 2 June 2008
Received in revised form
24 November 2008
Accepted 25 November 2008
Available online 6 December 2008

Keywords:
Rare earth alloys and compounds
Nanostructured materials

ABSTRACT

Tetrapod-shaped EuSe nanocrystals were prepared through the thermal reduction of europium chloride an organic selenide complex, n-hexadecylamine, and two additives oleic acid and oleylamine. The obtained EuSe nanoparticles were characterized by X-ray diffraction (XRD). The crystal grain size from the XRD spectrum was estimated to be 50 nm. In contrast, observation of the transmission electron microscope (TEM) gave larger sized EuSe (average size: 200 nm). Anisotropic crystal-growth of EuSe nanocrystals was achieved by addition of a small amount of oleic acid in the crystal growth process.

1. Introduction

Europoium chalcogenides (EuO, EuS and EuSe) are characteristic semiconductors which have the localized 4f electrons distributed between the conduction band (5d orbitals of Eu(II)) and the valence band (2p (O^{2-}), 3p (S^{2-}) and 4p (Se^{2-}) orbitals) [1–3]. The 4f–5d electronic transition and spin configuration of europium(II) chalcogenides are responsible for large Faraday and Kerr effects, which make them promising candidates for active materials in magneto-optical devices [4–10]. These magneto-optical properties are strongly dependent on their sizes [9]. Especially the photophysical properties of nano-sized materials are affected by size, shape, surface conditions and surrounding environment of the crystals [11,12].

It is known that size affects magneto-optic properties of nano-sized europium chalcogenides. Recently, we have reported on the enhancement of EuSe nanocrystals' magneto-optical properties, which are significantly dependent on the size and shape of each crystal [12]. These crystal grain sizes were calculated using the Scherer equation based on their XRD spectrum, and were estimated to be 11 and 20 nm. The saturation magnetization of EuSe nanocrystals was less than the expected value of 7.0 μ_β for the $^8S_{7/2}$ state of Eu(II). The disorderly arrangement of tiny crystal on the surface of the nanocrystals caused a decrease in the exchange interaction between Eu(II) ions. Thus, the large saturation magnetization of EuSe nanocrystals for magneto-optical devices requires a novel process for crystal growth of nano-scaled EuSe crystals.

Here, we report on the crystal growth of nano-scaled EuSe crystals by using specific additives, oleic acid and oleylamine, for the first time. The crystal growth of EuSe nanocrystals was achieved by way of europium nitrate with organic selenium compound and the additives (Fig. 1). We also prepared EuSe nanocrystals without the additives in order to compare the crystal growth. The EuSe nanocrystals were characterized by XRD and TEM measurements. It was concluded that the crystal growth process of EuSe nanocrystals could be developed in order to optimize nano-scaled magneto-optical materials.

2. Experimental

2.1. Apparatus

^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, and ^{31}P NMR data were measured by a JEOL AL-300 (300 MHz) and ECP-400 (400 MHz) spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were determined using tetramethylsilane (TMS) as an internal standard. ^{13}P NMR chemical shifts were determined using H_3PO_4 as an internal standard. Elemental analyses were performed with a PerkinElmer 2400II CHNS/O. Microwave induced plasma mass spectrometry (MIP-MS) were recorded on a HITACHI P-6000. High-resolution images of the EuSe nanocrystals were obtained with a Hitachi JEM-3100FEF TEM equipped with a tilting device (10°) and operated at 300 kV.

2.2. Materials

Europium(III) chloride hexahydrate ($EuCl_3{\cdot}6H_2O$) (99.95%) was purchased from Kanto Chemical Co. Inc. Selenium powder (99.9%) was purchased from Nakalai tesque. Inc. 1-Hexadecylamine (HDA) (90%) was obtained from Tokyo Chemical Industry Co., Ltd. Oleic acid (99%) and Oleylamine was purchased from Wako Pure Chemical Industries, Ltd. Potassium diphenylphosphide (5 M) in tetrahydrofuran

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doi:10.1016/j.jallcom.2008.11.126

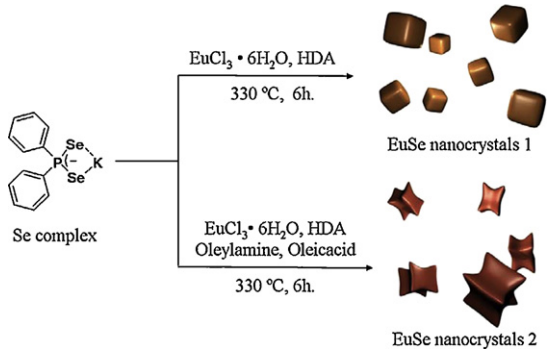

Fig. 1. Reaction schemes of EuSe nanoparticles 1 and 2.

was obtained from Aldrich Chemical Co., Inc. All other chemicals were reagent grade and were used as received.

2.3. Preparation of potassium diphenylphosphinediselenide $K(Se_2P(C_6H_5)_2)$

Potassium diphenylphosphinediselenide was following the reported method [12]. Yield: 74%. ^{1}H NMR (CD_3SOCD_3) δ = 8.02 (m, PC_6H_5 4H), 7.24 (m, PC_6H_5 6H) ppm. ^{13}C NMR (CD_3SOCD_3) δ = 130.87, 130.72, 128.30, 128.25, 126.77, 126.61 ppm. ^{31}P NMR (CD_3SOCD_3) 24.02 ppm. ESI-MS: 344.88. Anal. Calcd for $C_{12}H_{10}KPSe_2$: C, 37.71; H, 2.64%. Found: C, 36.75; H, 2.66%.

2.4. Preparation of EuSe nanocrystals 1

A solution of $K(Se_2P(C_6H_5)_2)$ (0.45 g, 1.2 mmol) in acetonitrile (10 ml) was added to $EuCl_3{\cdot}6(H_2O)$ (0.2 g, 0.44 mmol) dissolved in acetonitrile (30 ml) by stirring under nitrogen atmosphere for 2 h. The reaction mixture was concentrated, and hexadecylamine (HDA: 6.0 g, 25 mmol) was added at 330 °C under nitrogen atmosphere. After the reaction for 6 h, the resulting powder was cooled to room temperature. This powder was separated by centrifugation and washed with *n*-hexane. After washing, a brown powder was obtained.

2.5. Preparation of EuSe nanocrystals 2

A solution of $K(Se_2P(C_6H_5)_2)$ (0.45 g, 1.2 mmol) in acetonitrile (10 ml) was added to $EuCl_3{\cdot}6(H_2O)$ (0.2 g, 0.44 mmol) dissolved in acetonitrile (30 ml) by stirring under nitrogen atmosphere for 2 h. The reaction mixture was concentrated, and HDA (6.0 g, 25 mmol), oleylamine (0.67 g, 2.5 mmol) and oleicacid (0.70 g, 2.5 mmol) was added at 330 °C under nitrogen atmosphere. After the reaction for 6 h, the resulting powder was cooled to room temperature. This powder was separated by centrifugation and washed with *n*-hexane. After washing, a red powder was obtained.

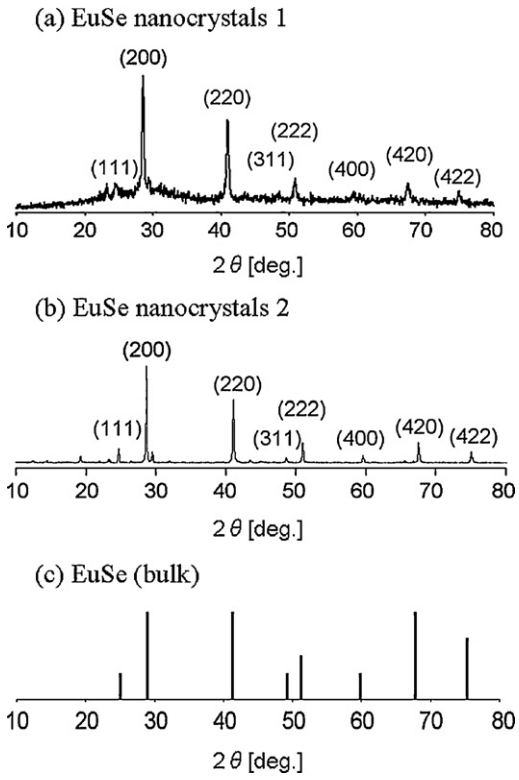

Fig. 2. XRD profiles of (a) EuSe nanoparticles 1; (b) EuSe nanoparticles 2; and (c) EuSe bulk.

2.6. Results and discussion

The formation of EuSe nanocrystals was carried out in situ generated europium diselenophosphinate compounds with HDA, oleylamine and oleicacid. The XRD pro-

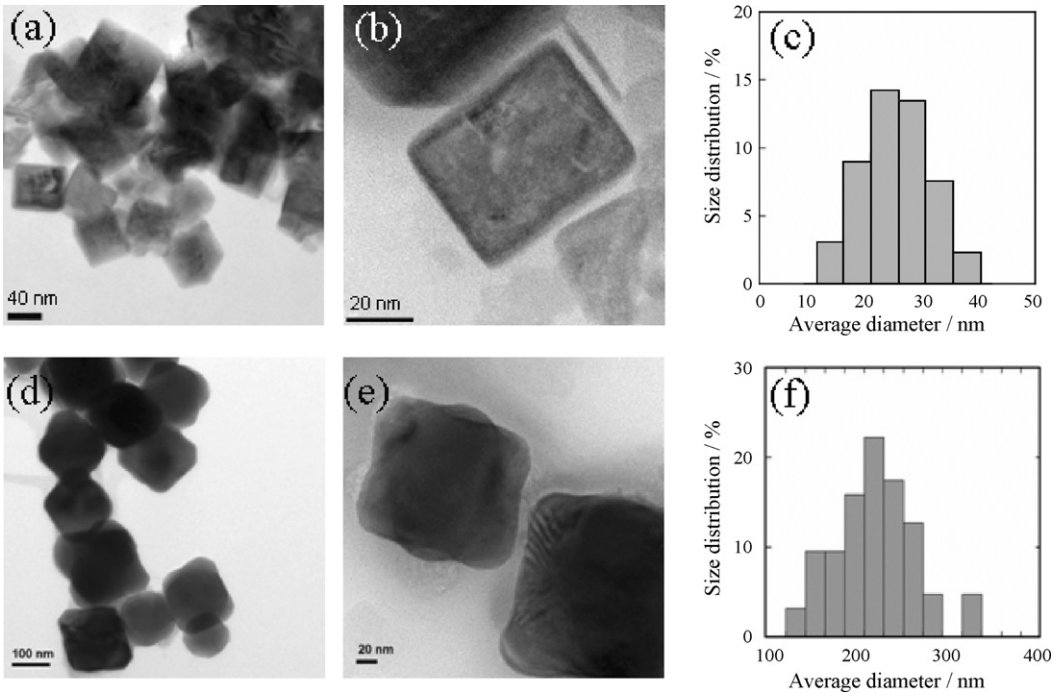

Fig. 3. TEM images of EuSe nanocrystals: (a and b) high-resolution TEM images of EuSe nanocrystals 1; (c) size distribution histogram of EuSe nanocrystals 1; (d and e) high-resolution TEM images of EuSe nanocrystals 2; and (f) size distribution histogram of EuSe nanocrystals 2.

files of crystalline EuSe nanocrystals 1 and 2 are shown in Fig. 2. Diffraction peaks $2\theta = 24.5^\circ, 28.6^\circ, 41.0^\circ, 48.6^\circ, 51.0^\circ, 59.5^\circ, 67.4^\circ$ and 75.0° were assigned to the (1 1 1), (2 0 0), (3 1 1), (2 2 2), (4 0 0), (4 2 0) and (4 2 2) planes of NaCl type EuSe, respectively. The intensity ratio of the diffraction patterns agreed with those of the bulk EuSe. We evaluated the fwhm (full width at half-maxim) of $2\theta = 28.6^\circ$ (2 0 0), which corresponds to the Bragg diffraction using the EuSe (2 0 0) plane. The crystal grain EuSe nanocrystals 1 and 2 were calculated using the Scherer equation from the XRD spectrum, and were found to be 20.5 and 51.0 nm, respectively. The XRD signals of EuO, Eu_2O_3, and Eu_2Se_3 were not observed in the XRD spectra of EuSe nanocrystals 1. However, in XRD signals of EuSe nanocrystals 2, we found that we observed the signals at around 20° and 30° that were not assigned to EuSe signals. The signal at around 30° is similar to that of $EuSe_2$ (30.18°) [12]. We propose that the small $EuSe_2$ might be existed on the surface of EuSe nanoparticles 2. We also observed that the XRD spectrum of organic capping ligands (HDA) gave the signals at around 20° [12]. Typical TEM images of EuSe nanocrystals 1 are shown in Fig. 3a and b. According to EuSe nanocrystals 1, the aspect ratio between the long and short sides of the rectangular particles was evaluated for 300 nanocrystals. The average aspect ratio was about 1.1, indicating well-ordered cubic nanocrystals. The average crystal size evaluated by the TEM observations was found to be 23 nm, and similar to the size measured by XRD (20.5 nm). The characteristic cubic shapes might be due to the NaCl-type fcc-structure of the EuSe lattice. On the other hand, we observed anisotropical crystal growth of the EuSe nanocrystals 2 from the images of TEM measurements (Fig. 3d). The average size was found to be 200 nm, and we obtained the characteristic "tetrapod-shapes" of the EuSe nanocrystals 2. These results indicated that the EuSe nanocrystals 2 were constructed by concentration of EuSe nanocrystal blocks (grain size = 50 nm).

The crystal growth and characteristic shapes of EuSe nanocrystals 2 are directly linked to the addition of oleic acid and oleylamine. In the first step of crystal growth, Eu(III) precursor complexes formed by coordination of organic-selenide ligands. However, we found that Eu(III) complexes with organic selenide ligands are unstable under air coordination, decomposing to Eu(III) ions and selene powder. Stabilizing the Eu(III) precursor complexes in HDA might be a key process for crystal growth of EuSe. We consider that carboxyl groups of oleic acid would play an important role in stabilizing of the Eu(III) precursor complexes. Eu(III) precursor complexes might be stabilized with oleic acid. The coordination ability of the carboxyl group is stronger than that of HDA. Oleylamine would also support the stabilization of the Eu(III) precursor in HDA. We propose that the crystal growth of EuSe nanocrystals 2 is due to formation of stable Eu(III) precursor complexes as a result of adding oleic acid and oleylamine.

3. Conclusion

In summary, we have succeeded in growing crystals of nanoscale EuSe by adding of oleylamine and oleicacid for the first time. To the best of our knowledge, the present study is the first report on the synthesis of starpod-shaped EuSe nanocrystals and the successful manipulation of EuSe nanocrsytal size. We expect that EuSe nanocrystals will have varied size when other additives are applied during crystal growth. We suggest that the crystal growth of EuSe depends on the coordination ability of the organic capping ligands. The coordination ability of carboxyl group in oleic acid might be stronger than that of corresponding amine group in HDA. The size and shape-controlled lanthanide nanocrystals are expected to open up pioneering fields in nano/micro materials, chemistry and magneto-optic science.

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