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The first observation of the magnetic circular dichroism in EuS nanocrystals

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Abstract

EuS nanocrystals were prepared by the liquid ammonia method. The size effect of EuS nanocrystals was observed in the magnetic measurements, the absorption spectra and the MCD spectra.

Keywords: Nanostructure; Semiconductor; Magnetic measurement

1. Introduction

There has been significant interest in the ferromagnetism of europium chalcogenides from the viewpoint of the ideal Heisenberg model. The chalcogenides (EuO and EuS) have 4f orbitals that exist as the degeneracy levels between the conduction band (5d orbitals of Eu(II)) and the valence band (2p orbitals of O^{2-} or 3p orbitals of S^{2-}) [1]. The spin moments of Eu(II) ions come from the 4f electrons [2,3].

We reported the preparation of EuS nanocrystals (average size of 20–40 nm) by use of liquid ammonia [4]. It is known that crystal size affects opto-magnetic properties [5–7] of europium chalcogenides. However, the size contribution to the opto-magnetic properties has not been clear yet. We propose that the spectral analysis of EuS nanocrystals in magnetic field is directly connected to understanding of the properties depending on their sizes.

Here, we have attempted to observe the absorption spectra of EuS nanocrystals under magnetic field using magnetic circular dichroism (MCD). MCD is a useful tool for information on the excited states connected with the ground states through the magnetic interactions [8].

In this work, the spectroscopic and magnetic properties of EuS nanocrystals have been examined systematically (size: 18, 29 and 36 nm). We report the characterization, the magnetic properties, the absorption spectra and the MCD analysis of the EuS nanocrystals.

2. Experiment

2.1. Materials

Europium metal (Eu 99.9%) was obtained from Sterm Chemicals. Hydrogen sulfide (pure H_2S) and ammonia (NH_3 99.9%) were purchased from Sumitomo-seika and Iwatani-neriki, respectively. The standard europium solution (1000 ppm) and sodium sulfate anhydrous (Na_2SO_4 99.0%) were purchased from Wako. All of the chemicals were reagent grade and were used as received.

2.2. Preparation of EuS nanocrystals

Europium metal (0.3 g) was added to liquid ammonia (50 mL, −78 °C) in a reaction flask. The color of the solution turned into deep blue with the dissolution of europium. H_2S gas was introduced into the solution through bubbling until

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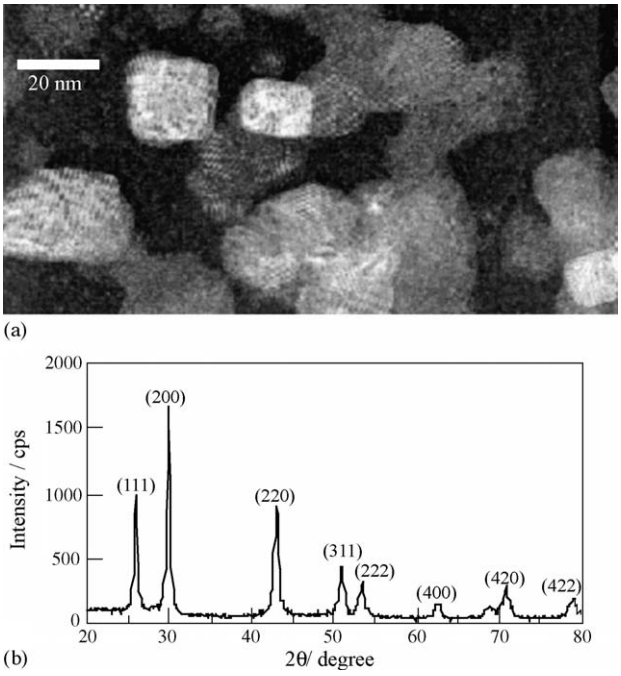

Fig. 1. (a) TEM images and (b) XRD spectra of the EuS nanocrystals with 18 nm particle size.

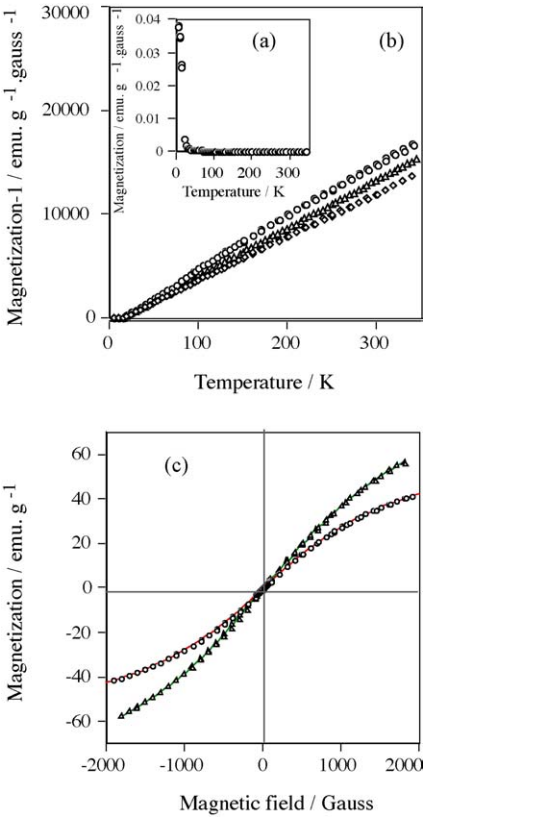

Fig. 2. (a and b) Correlation between magnetization (M) and temperature (T) under magnetic field of 100 Gauss with 18 nm (◯), 29 nm (△) and 36 nm (□) particle size; (c) correlation between magnetization (M) and magnetic field (H) at 10 K, of the EuS nanocrystals.

the color of the solution changed to yellow. Liquid ammonia was removed by evaporation at room temperature in 1.5 h. The resulting product was purple-black powder. The samples with various sizes were prepared by controlling evaporation rate of liquid ammonia.

2.3. Apparatus

X-ray diffraction patterns were recorded on a Rigaku X-ray Diffractrometer Multiflex using monochrometer Cu Kα radiation. The measurement conditions were 40 kW/40 mA, scan speed 3°/min, sampling width 0.1°, in air at room temperature. Transmission electron microscopy (TEM) images were obtained with a Hitachi H-9000 TEM equipped with a tilting device (±10°) and operating at 300 kV (C_S = 0.9 nm)

UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer at room temperature. MCD spectra were measured on a JASCO J-720W spectrolarimeter. The Faraday effect spectra were measured on JASCO Model K-250. Magnetic susceptibility data were obtained between 2 and 300 K by using a SQUID susceptometer (MPMS-5S, Quantum Design).

3. Results and discussion

3.1. Characterization of EuS nanocrystal

The TEM image of EuS is shown in Fig. 1a. In the TEM images, we found square-shaped crystals of EuS.

The XRD spectrum of the sample is shown in Fig. 1b. The diffraction peaks 2θ = 25.9°, 30.0°, 43.0°, 50.8°, 53.4°, 62.3°, 70.9° and 79.0° of the sample were assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 0) and (4 2 2) planes of NaCl type of EuS. The crystal sizes of the samples were calculated by the Scherer equation from the X-ray diffraction (XRD) spectra, and were found to be 18, 29 and 36 nm.

3.2. Magnetic properties

Temperature dependencies of the magnetization are shown in Fig. 2a. On lowering the temperature, the magnetization products became larger according to the Curie law (300–15 K), and the Curie points of the samples (16 K) were the same order as that of bulk EuS as shown in Fig. 2b. However, we observed that the magnetic moments of 18 nm EuS nanocrystals was smaller than those of corresponding 29 and 36 nm EuS. The correlation between magnetization (M) and magnetic field (H) at 10 K in the EuS nanocrystals is also shown in Fig. 2c. The saturation magnetization of the EuS nanocrystals is increased with increasing the size.

We proposed a mechanism of the magnetization supported by a paper [2] reporting that the magnetization of Eu chalco-

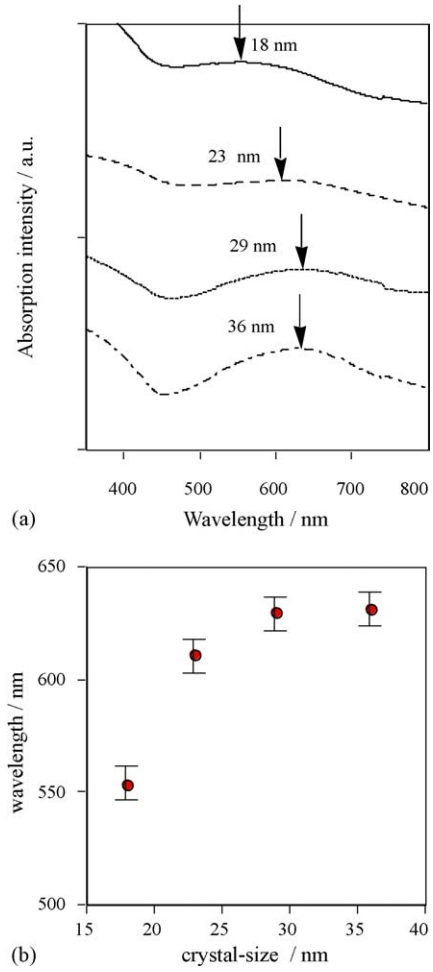

Fig. 3. (a) Absorption spectra of EuS nanocrystals (18, 23, 29 and 36 nm particle size) at room temperature. (b) Correlation between the crystal-size and the peak top of the 4f–5d transitions.

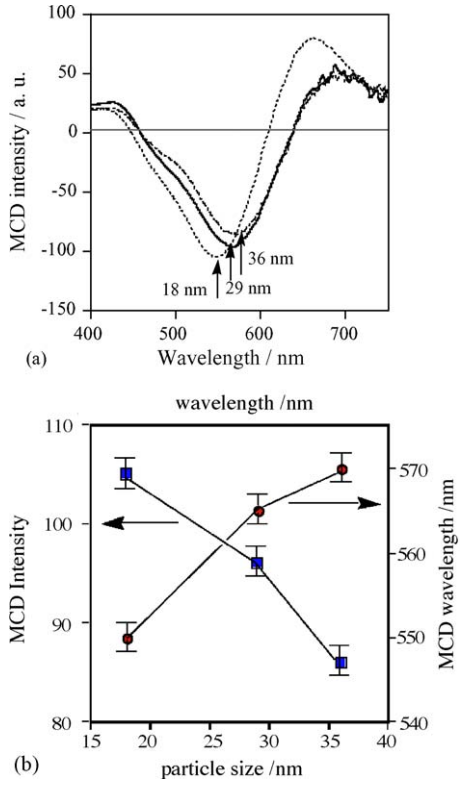

Fig. 4. (a) Correlation between the crystal-size and the peak top of the 4f–5d transitions of MCD spectra with 18, 29 and 36 nm particle size in DMF at room temperature. (b) Correlation between the particle size (◯) and the MCD peak top intensity (□).

genides crystals with fcc structure depends on the distance between the two Eu ions. The ratio of the nearest neighbor Eu(II) to the next nearest one (*i*/*j*) should be related to the average distance between the Eu cations. According to the rocksalt (fcc) structure of EuS, each Eu(II) ion has 12 nearest neighbor ions (*i*: ferromagnetic interaction) and 6 next-nearest neighbor ions (*j*: antiferromagnetic interaction). Both positive and negative exchange interaction are present. A positive (ferromagnetic) interaction occurs between the nearest neighbors and a negative (antiferromagnetic) interaction does between the next-nearest neighbors. Smaller crystals size leads to decrease of *i*/*j*, resulting in smaller magnetic moment.

3.3. UV–vis absorption and MCD spectra analysis

The absorption spectra with various particle sizes (18, 29 and 36 nm) of EuS at room temperature are shown in Fig. 3a. The absorption spectra around 650 nm of the EuS nanocrysatals originates from $^4f_7(^8S_{7/2}) \rightarrow {}^4f_6(^7F_J)5d(t_{2g}, e_g)$ electron transition of Eu(II). In Fig. 3b, the peak top wavelength of the absorption of the EuS nanocrystals shifted to shorter wavelength with decreasing the sizes.

The MCD spectra with various particle sizes (18, 29 and 36 nm) of EuS in DMF at room temperature are shown in Fig. 4a. The shape of the MCD spectra was the typical type. All of EuS exhibited the same MCD pattern structures, and the positive and negative MCD peaks around 500–600 nm of EuS were assigned to 4f–5d transitions.

The crystal-size dependences of the intensities and wavelength at the top of the MCD spectra of the EuS nanocrystals are shown in Fig. 4b. The MCD intensity was normalized by the oscillator strength in order to characterize opto-magnetic properties of EuS. In Fig. 4b, the peak top wavelength of the MCD of the EuS nanocrystals shifted to shorter wavelength with decreasing the sizes. In contrast, the intensities of the MCD of the EuS increased with the decreasing the crystal size (Fig. 4b).

Smaller particle size leads to increasing of the "terminal-Eu(II)" on the crystal surface. Physical properties of the "terminal-Eu(II)" on the crystal surface should be much different from that of the "inner-Eu(II)" in the crystals. The opto-magnetic effect of the surface Eu^{2+} ions might be stronger than that of the inner Eu^{2+} ions.

4. Conclusions

We have observed that the magnetic moments and the magnetization of EuS nanocrystals decreased with decreasing the crystal-size.

Dependence of the MCD intensity on the crystal-size has been observed for the first time for EuS. Decreasing the size of the EuS led to the enhancement of the MCD intensity. These behaviors resulted from the physical properties of the "terminal-Eu(II)" on the crystal surface should be much different from those of the "inner-Eu(II)" in the crystals.

The size dependences of magnetization were different from that of the MCD intensity. Further studies on the VT-MCD and synthesis of the EuS less than 15 nm are in progress in our laboratory.

The size-controlled EuS nanocrystals would be a promising material for opto-magnetic device in the future.

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