Liquid Phase Synthesis of EuS Nanocrystals and Their Physical Properties[6)]

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Introduction

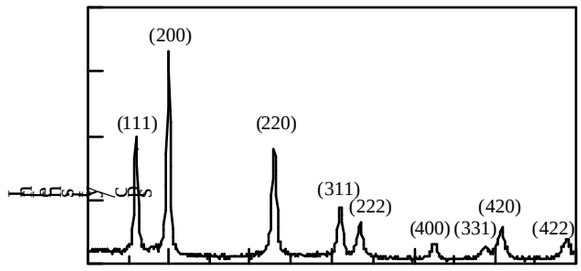
It is known that crystal size affects optomagnetic and luminescent properties of europium chalcogenides.[1-3)] By use of liquid phase reaction, we succeeded in preparing the first EuO nanocrystals4) and found that the magnetic susceptibility in EuO nanocrystals increased upon an irradiation of UV light.[3)]

In this work, we report a novel method for preparation of high quality EuS nanocrystals using gaseous H_2S in liquid ammonia. We have identified EuS nanocrystals and obtained essential physical properties by XRD, TEM, ICP-ES, FT-IR and UV-Vis. Furthermore, we observed that the change of their magnetic properties might depend on the morphology of the nanocrystals.

Experiment

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 as dissolution of europium. H_2S gas was introduced into the solution through bubbling until the color of the solution changed into yellow. Liquid ammonia was removed by evaporation at room temperature in 1.5 h. The resulting product was purple-black powder.

XRD measurements demonstrated well-crystallized structure of the sample (**Figure 1**). Diffraction peaks were assigned to the planes of NaCl type EuS. The average size of EuS was calculated by the Scherer equation was 20.4 nm. The reaction mechanism is shown in **Scheme 1**. After addition of europium metal to liquid ammonia, the color of the solution turned to deep blue because of the formation of solvated electrons ($e^{-ammonia}$) and Eu(II) ions **(1)**. H_2S gas diluted with argon was introduced to the solution through bubbling, resulting in an immediate color change into yellow. In liquid ammonia, H_2S acts as an acid that dissociated into HS^- and S^{2-} **(2, 3)**. The yellow color was observed after introduction of H_2S. The purple-black color of EuS from the reaction of Eu(II) and S^{2-} was observed after evaporation of liquid ammonia **(5)**. UV-Vis absorption of the EuS nanocrystals shifted to shorter wavelength compared with the reported EuS film (**Figure 2**).[3)] The blue shift is mainly caused from effects of crystal environment to *f-d* transition of Eu(II) ions and partly from size effect. The nanocrystals showed the same Curie point (16.6 K) as the bulk EuS (**Figure 3**). More details of physical properties of the EuS nanocrystals will be discussed in the conference.

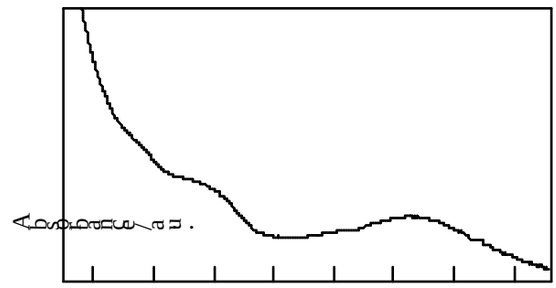


2θ / degree

Figure 1. XRD patterns of the EuS nanocrystals.

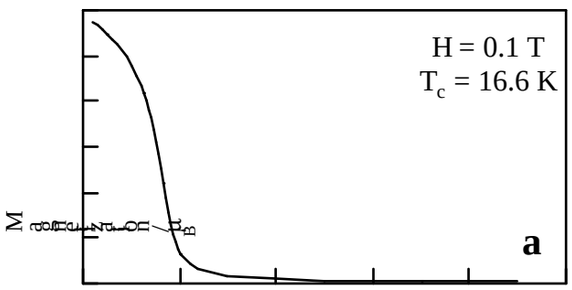
$$Eu(0) + NH_3 \longrightarrow Eu(II) + 2\,e^{-ammonia} \quad (1)$$
$$H_2S + NH_3 \longrightarrow HS^- + NH_4^+ \quad (2)$$
$$HS^- + NH_3 \longrightarrow S^{2-} + NH_4^+ \quad (3)$$
$$NH_4^+ + e^{-ammonia} \longrightarrow 2NH_3 + 1/2H_2 \quad (4)$$
$$Eu(II) + S^{2-} \longrightarrow Eu(II)S \quad (5)$$

Scheme 1. Reaction mechanism



Wavelength / nm

Figure 2. UV-Vis absorption spectrum of the EuS nanocrystals.



Temperature / K

Figure 3. (**a**) Correlation between Magnetization (**M**) and Temperature (**T**) under magnetic filed of 0.1 T of the EuS nanocrystals.

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