Spindle-Type EuO Nanocrystals and Their Magnetic Properties

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EuO nanocrystals were prepared by liquid phase reaction of europium metal in liquid ammonia for the first time. TEM revealed that the EuO nanocrystals had a spindle shape with mean length of 280 nm (*a*) by mean width of 95 nm (*b*). The SQUID measurement showed that the EuO nanocrystals turned into ferromagnetic phase at 70 K and 150 K.

Europium(II) oxide (EuO) is a magnetic semiconductor which presents a paramagnetic phase at temperatures above the Curie temperature (T_c = 70 K). The seven *f* electrons that locate between the valence band (*2p* of O^{2-}) and the conduction band (*5d* of Eu^{2+}) in EuO lead to the *4f–5d* transition and optomagnetic properties such as Faraday and Kerr effects.[1–5] EuO is a promising material for optical isolators and optomagnetic devices because of its unique magnetic properties.

EuO has been prepared by the solid phase reaction of Eu_2O_3 with europium metal at high temperature (>1000 °C) since 1960s.[6,7] In contrast, liquid phase reactions are advantageous in preparation of nano-scaled semiconductors, especially quantum dots, because solvent molecules work as surface-modification regents, and prevent aggregation of the particles.[8] The theoretical quantum confinement model predicts the unique magnetic properties of EuO nanocrystals.[9,10] Keeping these points in our minds, we have successfully prepared the nanostructure of EuO in liquid ammonia for the first time. Furthermore, we also reported the magnetic properties of EuO nanocrystals.

Europium metal (0.2 g) was added to liquid ammonia (20 mL) under nitrogen atmosphere. The color of the solution turned to deep blue because of generation of solvated electron ($e^-_{ammonia}$) and Eu(II) ions.[11,12] Oxygen diluted with argon was introduced to the solution through bubbling. The formation of Eu(II)O is shown as Scheme 1.

$$\begin{aligned} &Eu(0) + NH_3 \longrightarrow Eu(II) + 2\,e^-_{ammonia} \\ &2e^-_{ammonia} + 1/2\,O_2 \longrightarrow O^{2-} + 2NH_3 \\ &Eu(II) + O^{2-} \longrightarrow Eu(II)O \end{aligned} \quad (1)$$

After disappearance of the blue color, the system was warmed to room temperature to remove the excess ammonia. The crude product was washed with HCl (0.01 mol dm^{-3}) solution, deionized water, and methanol, and dried in vacuum (10^{-2} Torr; 1 Torr = 133.3 Pa) to give a grayish white powder. The obtained europium compound was identified by the electron diffraction pattern of TEM. The electron diffraction patterns of the nanocrystals were observed to be *d* = 2.96, 2.56, 1.81, 1.48, 1.29, 1.16 and 0.98 Å, which agreed to the *d* values of (111), (200), (220), (222), (400), (420) and (511) planes of NaCl-type EuO, respectively (Figure 1). The nano-scaled EuO consisted of spindle-shaped nanocrystals with mean length *a* of 280 nm by mean width *b* of 95 nm (Figure 2). The wider size distribution of *a* dimension gave us an idea that the crystals growth proceeded faster in direction *a* than *b* in liquid ammonia. A conceptual mechanism of the crystal growth is depicted as Figure 3. First, europium metal dissolves in liquid ammonia to give a europium precursor complex. The strong coordination of ammonia molecules on *d* orbitals of Eu(II) ion would affect on the orientation of the precursor complex so that the complex reacts with oxygen to yield spindle-shaped EuO nanocrystals.

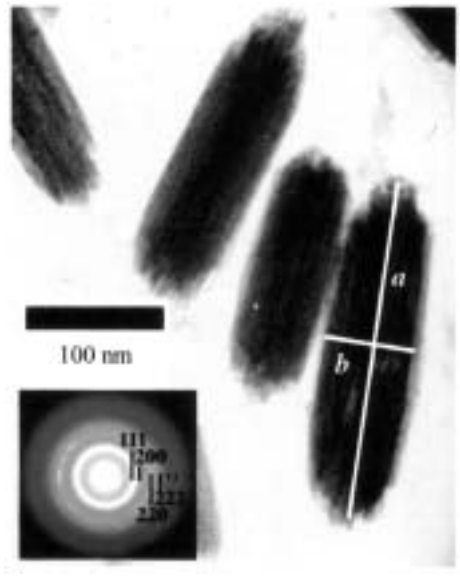

Figure 1. TEM image and electron diffaction patterns (inset) of EuO nanocrystals.

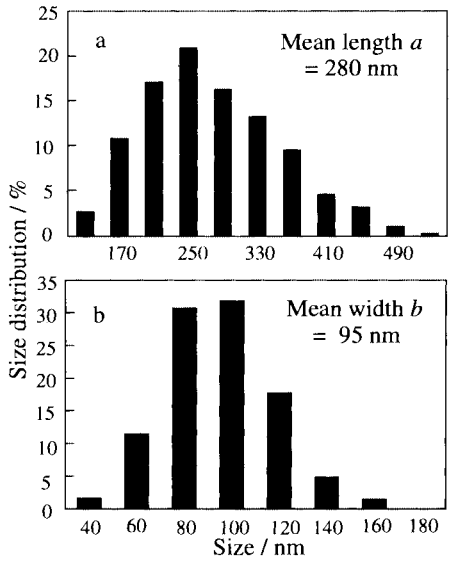

Figure 2. Size distribution of the EuO nanocrystals in (a) length *a* and in (b) width *b*.

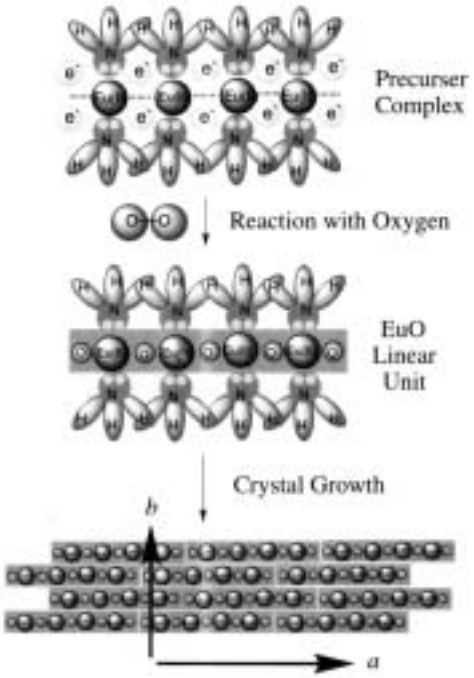

Figure 3. Postulated machanism of the crystal growth.

The temperature dependence of magnetic susceptibility (χ) of the EuO nanocrystals was measured by SQUID (Superconducting Quantum Interface Device). We observed two magnetoactive phases in the EuO nanocrystals and Curie points were observed at 70 K and 150 K (Figure 4(a)). These Curie points were similar to the values reported for EuO films (thickness = 0.5–1 μm) with oxygen vacancies.[13–14] The appearance of T_{c_2} is caused from a large amount of oxygen vacancies that formed magnetic impurity states. The number of oxygen vacancies of our EuO nanocrystals would be as high as in micro-sized EuO films (5–7%).[13–14] The effective number of Bohr magneton μ_{eff} of EuO nanocrystals was estimated to be 8.27 (μ_{eff} of Eu(II) = 7.94). The correlation between magnetic field and magnetization of EuO nanocrystals gave hysteresis with coercive force $H_c = 8.72 \times 10^{-3}$ T (Figure 4(b)). Fishel and co-workers reported the synthesis of EuO using liquid ammonia (–78 °C) in 1970, however, they obtained bulk EuO identified by XRD (X-ray Diffraction) after heat treatment at 850 °C.[15]

In conclusion, we successfully prepared EuO nanocrystals in liquid ammonia for the first time. To the best of our knowledge, the liquid phase reaction is the only simple way to obtain EuO nanocrystals at present. The liquid phase reaction is a promising way to give smaller particles of EuO nanocrystals with higher Curie points for practical optomagnetic materials in near future.

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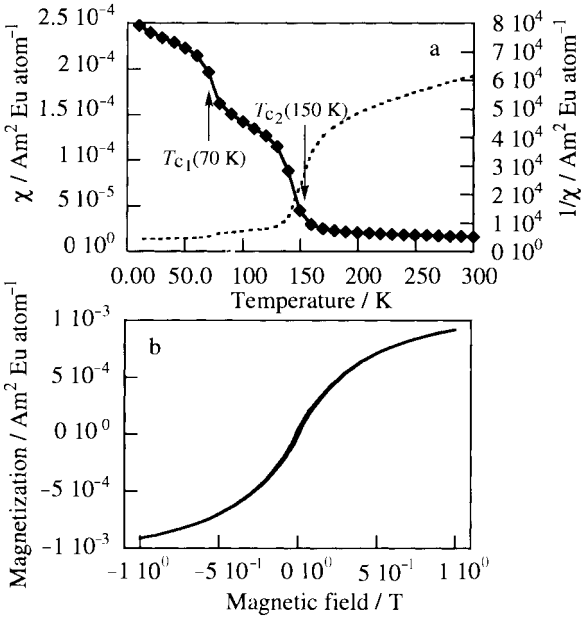

Figure 4. (a)Temperature dependence of Magneic susceptibitly χ under applied field 0.1 T and (b) magnetic filed dependence of magnetization at 10 K of EuO nanocrystals.

References and Notes

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