The Study of a Quantum Confinement Model of EuO Nanocrystals Using X-ray Absorption Spectroscopy

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Abstract

Europium Oxide (EuO) has been investigated as a new promising magnetic material for recording media applications. The quantum confinement structures of EuO nanocrystals are investigated by synchrotron spectroscopy techniques. We study the qualification of nanocrystals on the following: the physical structure, optical property, electronic band structure and atomic structure of nanocrystals. EuO-nanocrystals have been synthesized by dissolving Eu-metal in liquid ammonia and oxidizing Eu^{2+}-ions solution with oxygen gas within absolute vacuum conditions. The powder of sample is identified. The physical structures of nanocrystals are studied using an XRD technique. Moreover, we use the image of SEM and TEM to study the lattice fringes and average crystals size of EuO. The optical property and electronic band structure are studied using the XANES technique. The spectra of XANES show the specific absorption energy of each atom. In this paper, we are interested in studying the L_3-edge energy of Eu^{2+}. The atomic structure of nanocrystals is indicated using the EXAFS technique. The spectra of EXAFS are used to explain the type of center atom, number of neighbor atoms and the length between the center atom and neighbor atoms. Both XANES and EXAFS analyses are the combination signal from the XAS spectroscopy technique that is conducted by synchrotron light from the National Synchrotron Research Center (NSRC).

Keywords: Synchrotron light, Europium oxide, EuO, XRD, SEM, TEM, XAS, XANES, EXAFS.

1. Introduction

In 1961, EuO was discovered by B.T. Matthias et al. [1]. It has a crystallized rock-salt structure; at room temperature it is anti-ferromagnetic. For a variety of physical properties and applications, crystals of EuO have been studied for 40 years. In the past, the investigation mainly concentrated on bulk EuO properties, such as optical property and magnetic property. For instance, K.Y. Ahn et al. [2] discovered the Faraday Effect phenomenon that occurrs when the crystals are excited by an external magnetic field. Also, K. Kawaguchi et al. [3] found the magnetic switching property, with the Curie temperature of EuO, which is 69K. These phenomena lead the crystals of EuO to be recognized as a new magnetic material for development of the recording media industry.

New electronic devices can be built out of the electromagnetic switching theorem.

We know that the properties of EuO are strongly dependent on crystal-size. When the size of crystals is decreased, for example, the energy band is split, the Curie temperature decreases and the magnetization increases when the temperature is changed. We call these phenomena the quantum confinement properties. Thus, many scientists are interested in the properties of EuO-nanocrystals, such as luminescence property, emission property and photo-magnetic property. New spectroscopy technology and new instruments were used to analyze the crystals. For instance, V. Bocatius et al. [4] used HREELS spectroscopy to measure the energy loss of electrons by the vibration of crystals. Y. Hasegawa [5] used EPR measurement for showing the formation of
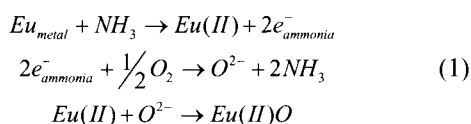
photo-active classes on EuO-nanoparticles. Finally, Q.H. Chen et al. [6] described the energy absorption and emission spectra of EuO-nanocrystals using UV-Vis spectrometer and fluorescence spectroscopy, respectively. Groups of scientists are interested in EuO crystals. Their properties in nanocrystals are more and more important, but the knowledge of overall properties is small.

The structure and the binding of metal atoms using the principle of X-ray absorption spectroscopy (XAS) presents a unique method to study the properties of materials. The XAS technique consists of two different techniques that are X-ray absorption near-edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) measurement. XANES allows for the recognition of a specific atom and is used to determine the oxidation state of an element. EXAFS also allows for the identification of the nearest neighboring atoms to the absorbing atom to determine the coordination environment for the metal of interest [7]. In this paper, we report the studies on preparation of the EuO-nanocrystals and the characterization of their properties using the XAS novel technique.

2. Experimental

Preparation of EuO Nanocrystals

The EuO-nanocrystals were prepared in a nitrogen atmosphere as follows: europium metal (0.5g) was added to liquid ammonia under N_2 atmosphere protecting the solution from the humidity of air. The color of solution becomes strong blue due to the reaction of solvent between an electron of ammonia ($e^-_{ammonia}$) and Eu(II)-ions. Next, oxygen gas diluted with argon was introduced to the solution through bubbling. The formation of EuO is shown as equation 1:

$$Eu_{metal} + NH_3 \rightarrow Eu(II) + 2e^-_{ammonia}$$
$$2e^-_{ammonia} + \frac{1}{2}O_2 \rightarrow O^{2-} + 2NH_3 \qquad (1)$$
$$Eu(II) + O^{2-} \rightarrow Eu(II)O$$

All processes were frozen with solid carbon-dioxide to condense nitrogen gas and oxygen gas. After the deep blue color of the solution disappeared, the system was warmed to room temperature to evaporate the extra ammonia. The coarse product was washed with HCl (0.1 mol/m^3) solution, de-ionized water, and methanol, and dried in vacuum to obtain a grayish white powder product.

XRD Measurement

The physical structure of EuO-nanocrystals verified the formation of Eu(III)-ions and Eu(II)-ions that was indicated by X-ray diffraction (XRD) measurement at 10° - 80°. XRD-pattern that was recorded on the JEOL JDX-3530 thata-2thata X-ray diffractometer from the National Metal and Materials Technology Center (MTEC-Thailand). The pattern was obtained using Bragg-Brentano geometry with CuKα-radiation as an X-ray source with an acceleration voltage of 30-kV, a beam current of 40-mA, scan speed of 1.2°/min. and sampling width 0.5° at room temperature.

SEM and TEM Measurement

We use SEM and TEM techniques to study the nanostructure of the sample. The JSM-5410 is an analytical SEM machine. It has a magnification of 20x-25,000x and an energy resolution of SiLi 133-eV. Also, it can differentiate the differential distance of 3.5-nm at 30-kV. Moreover, we use the JEOL-JEM-2010 for an analytical TEM machine. It has a LaB$_6$ electron gun and can be operated between 80-200 kV with point resolution of 0.23-nm. Also, it has both specimen holder single tilt and double tilt. This allows ultra-microarea x-ray analysis.

XANES and EXAFS Experiment

The optical properties and the electronic band structure of EuO-nanocrystals were studied by XANES measurement. The atomic structure of EuO-nanocrystals was studied by EXAFS measurement.

All spectra were recorded at the Eu-L$_3$ edge using synchrotron light from synchrotron light source equipped with 1.2-GeV maximum beam energy using a double bend achromatic storage ring, a beam current of 30-mA and RF frequency of 118-MHz in the RF cavity of 60-kV, with Si(311) double crystal monochromes from the National Synchrotron Research Center (NSRC) [4].
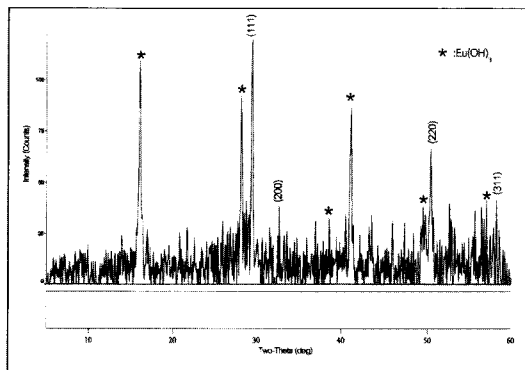
Fig.1 The XRD pattern of EuO-nanocrystals. The peaks at (111), (200), (220), (311) planes are identified for EuO.

XAS Data Analysis

We used IFEFFIT-1.2.9 software package to analyze the results of EXAFS data by standard methods. First, the raw data was calibrated on the edge energy by first or second degree derivative to indicate the inflection point of edge. After calibration, the pre-edge was subtracted by the 1st - 3rd degree of Spline polynomial or Victoreen polynomial removal fit curve. We found that the kinetic energy of photo-electrons were 6972.74(5)-eV. The EXAFS data was normalized and converted to wave vector (k) space. Next, the EXAFS curve in k-space was weighted by k^1, k^2 or k^3 and Fourier transformed (FT), which gave the radical structure function of the edge.

3. Results and Discussion
XRD Measurement

The XRD pattern shows the combination of crystalline phase and amorphous phase of EuO-nanocrystals. In addition, the XRD pattern described the mixture of EuO and $Eu(OH)_3$ crystalline structures. In Fig. 1, the diffraction peaks are at 2θ = 30.06(5), 34.85(5), 50.11(9) and 59.55(9) due to the (111), (200), (220) and (311) planes of EuO-nanocrystals and it shows that the structure of the crystals is the FCC rock-salt structure. The diffraction peaks are at 2θ = 16.08(2), 28.97(2), 37.45(4), 40.96(2), 49.72(3) and 58.16(5) due to the (100), (110), (111), (201), (300) and (112) planes, respectively. This describes the XRD pattern of $Eu(OH)_3$.

From equation 1, the Eu(II)-ions in liquid ammonia, being stable at low temperature, are dissolved by ammonia-ions until the color of the solution is changed to a deep blue color. In liquid ammonia, oxygen gas is reduced into O^{2-} ions. Then they react with the Eu(II)-ions and form EuO-nanocrystals. However, O^{2-} has a low reaction at low temperature and we knew that the NH_3 is separated into NH_2^- and NH_4^+ in liquid ammonia. So, the reaction of O^{2-} and H^+ might happen and give OH⁻ which form the $Eu(OH)_3$ in the XRD pattern [5].
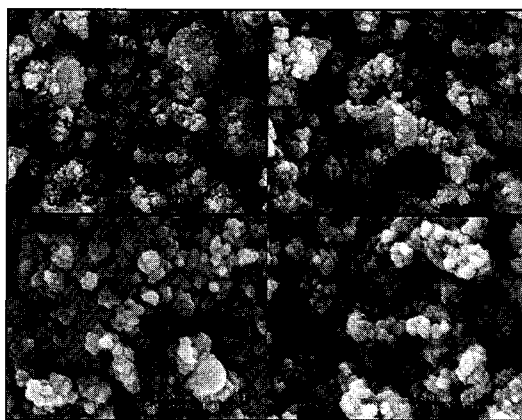

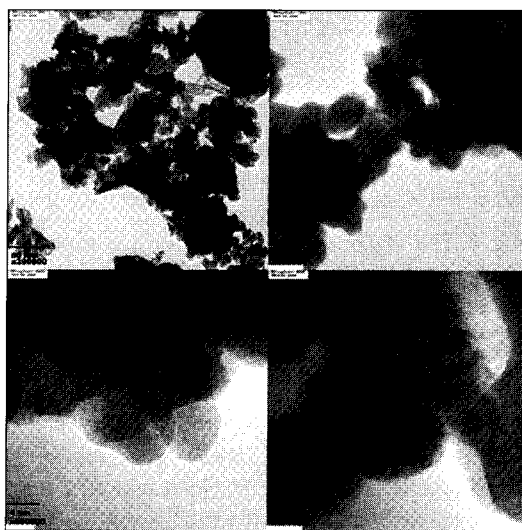**Fig.2** The SEM image of EuO-nanocrystals. The nanostructure of EuO is a group of grains.

Fig.3 The TEM image of EuO-nanocrystals. The average crystal size is 14-nm.

SEM and TEM Measurement

We use SEM and TEM to study the nanostructure of EuO. At low magnification power, the pictures of SEM are shown in Fig. 2. The physical structure of an EuO-nanocrystal is a group of small grains and the size of each grain is less than 1-μm. At high magnification power, the pictures of TEM are shown in Fig. 3. We successfully observed the clear lattice fringes, or d-space patterns, of the EuO-nanocrystals. The average size of crystals is found to be 14-nm.
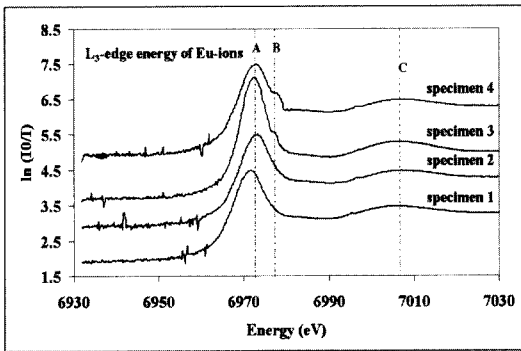
(a)
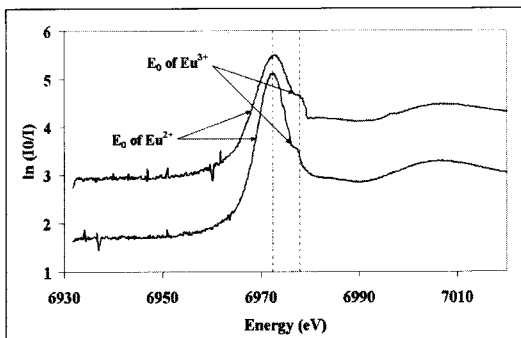
(b)

Fig.4 The XANES spectra of Eu-L_3 edge for EuO (a) show the peak energy of absorption atom and (b) show the inflection point of Eu^{2+} and Eu^{3+}.

XANES Measurement

To obtain overall information on the EuO-nanocrystals, such as local electronic structure, we used XANES technique to focus on L_3-edge energy of Eu^{2+}-ions, which are unaffected by oxygen-ions in the sample.

It is known that the X-ray absorption peaks, so-called white lines, appear at the higher energy side of the Eu-L_3 edge energy. The position of white lines is responsive to the environment of the chemical structure and very sensitive to the changing of the valence state. Therefore, the XANES technique is used to study the valence state of an absorption-ion. In Fig. 4(a), the XANES spectra have quite complex structures conditioned by contributions of X-ray absorption on europium-ions in a divalent state (Eu^{2+}), which is located at 6972.74(5)-eV (as shown at peak A). In addition, we found a weak white line component of Eu^{3+}-L_3 edge that is located at 6978.58(1)-eV (as shown at peak B). It could be confirmed that there is a mixed valence configuration between Eu^{2+} and Eu^{3+} in the sample, which conforms to the result of XRD-measurement.

We think that the result of XANES also shows the reduction of divalent Eu^{2+} into trivalent Eu^{3+} by the humidity of air in the preparation of EuO-nanocrystals. The peak energy values are very close to those of Eu^{2+} and Eu^{3+}, and refer to EuO and $Eu(OH)_3$, respectively, which are considered to be the transitions of electrons from the $2p_{3/2}$ (Eu-ions) valence state to the unoccupied-state with 5d-6s (O-ions) conduction state above the 4f (Eu-ions) Fermi energy level. In XANES spectra, the Valency value (V) is defined by equation 2:

$$V = \frac{2 + I_{Eu^{2+}}}{I_{Eu^{2+}} + I_{Eu^{3+}}} \qquad (2)$$

when the $I_{Eu^{2+}}$ and $I_{Eu^{3+}}$ are amplitudes of peaks corresponding to Eu^{2+} and Eu^{3+}, respectively.
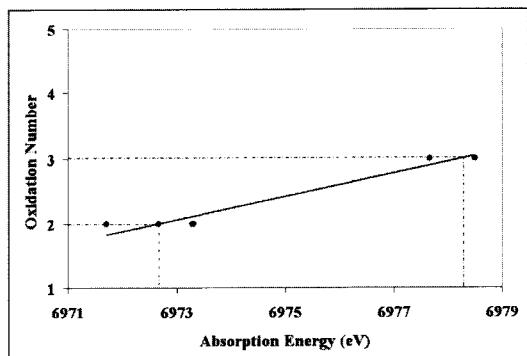

Fig.5 The relation between the oxidation number of Eu-chalcogenides and the absorption edge energy.

Moreover, the XANES spectrum is used to identify the inflection point of the Eu-L_3 edge energy that refers to the ionization energy (E_0) of Eu-ions. In Fig. 3(b), the E_0 values of Eu^{2+} and Eu^{3+} are 6968.67(7) eV and 6976.58(5) eV, approximately. Therefore, the energy of L_3 edge of Eu^{2+} is approximately 8.0-eV lower than the L_3 edge of Eu^{3+}, so Eu^{2+} ion is ionized easier than Eu^{3+} ion [5].

In Fig. 4(a), the white line at the peak C, produced by photoelectron scattering from the further atoms, located at 7007.89(1)-eV, appears as a small peak that refers to the smaller cluster size of EuO crystal. It also shows that there is at least one coordination atom around the absorption center atom.

Finally, from the XANES spectra, the absorption peak of Eu^{3+} is higher than the absorption peak of Eu^{2+}. Therefore, we conclude that the increasing of the oxidation number depending on the growing absorption edge energy of Eu-chalcogenides. Fig. 5 shows the linearly relation between the oxidation numbers and the edge energy. This graph is used to explain the oxidation number of Eu-chalcogenides at each of the absorption edge energies.
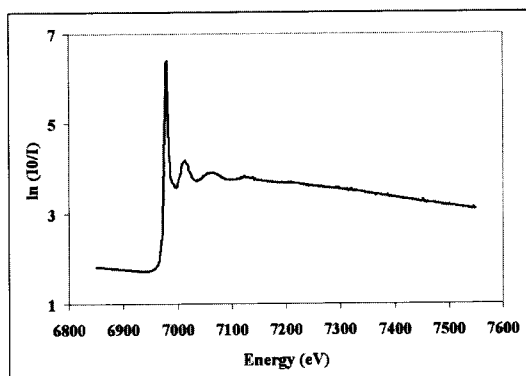
divalent and trivalent Eu-ions. So, it follows that the structure analysis by EXAFS is not clear and it is not expected to be reliable. Therefore, we carried out the structure analysis for a EuO-nanocrystal sample, where the dominant valence state of Eu is divalent. We were not concerned with the comparison of two different europium-species in this paper.

In addition, we might consider the EXAFS spectrum of nano-crystalline EO. The first effect is involved with the affect of grain size that attenuates the intensity of the signal in the normalized EXAFS spectra, as shown in Fig. 6. However, the reduction of EXAFS spectra might happen by the distortion of the spectra due to the self-absorption effect.
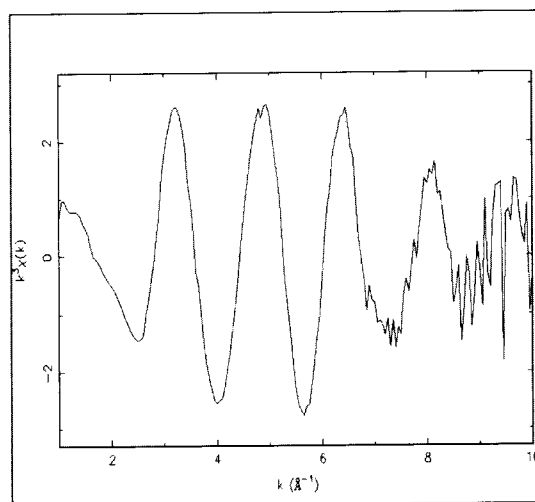

Fig.7 The k^3 χ(k) oscillation of Eu-L_3 edge of EuO.

Fig.6 The spectrum of EXAFS in raw file indicates the crystalline property of EuO-nanocrystal samples.

EXAFS Measurement

Structure analysis of EuO-nanocrystals

We used the EXAFS analysis to study the structure of EuO-nanocrystals. Due to the XRD-measurement, we found the sample consists of two different europium-species which are
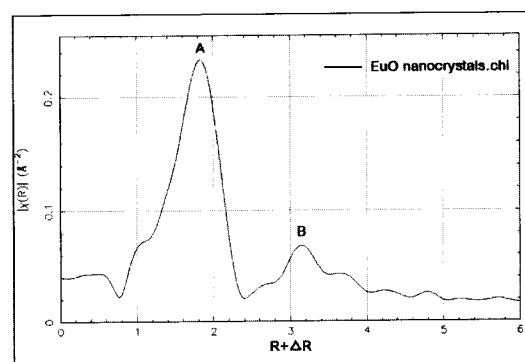

Fig.8 The FT of k-weighted EXAFS spectrum of EuO.

Fig. 7 shows k^3-weighted Eu-L$_3$ edge EXAFS spectra of EuO-nanocrystals. The spectra show that the distinct oscillation is in the range of $2 - 5$ Å^{-1} and the confusing oscillation is in the higher k-region (more than 6 Å^{-1}). This result is identical with other Eu-species that are around $2 - 7$ Å^{-1}. However, the prominent peak around 3 Å^{-1} is observed, while the peak is not observed in other species.

The local structure of Eu^{2+} became visually clearer when the Fourier transform is achieved on the k^3-weighted EXAFS spectra, as shown in Fig. 8. The peak appearing at 1.98(6) Å is attributed to $Eu \leftrightarrow O$ bond and the peak at 3.23(3) Å is attributed to $Eu \leftrightarrow Eu$ bond. In addition, the peaks, from the inter-atomic distances of 3.70(6) Å and so on, show the full multiple scattering oscillations of the next neighboring atoms.

Table 1 The summary of EXAFS results of EuO.

Sample	Correlation	N	R (Å)	σ^2 (Å^2)	R-factor
EuO	Eu-O	6	2.57	0.044	2.63
	Eu-Eu	12	3.63	0.044	3.69

Curve-fitting analysis

In order to analyze the details of the measure EXAFS spectra, curve fitting was carried out using theoretically calculated spectra with IFEFFIT 1.2.9 software. From Table 1, three parameters are chosen for each shell: coordination number (N), bond length (R) and Debye-Waller factor (σ^2).

The difference between $Eu \leftrightarrow O$ bond obtained from the EXAFS technique and the one obtained from calculation is about 0.59 Å, similarly the difference between $Eu \leftrightarrow Eu$ bond obtained from the EXAFS technique and the one obtained from calculation is about 0.42 Å. This is due to the size of the crystal decreasing according to the quantum confinement properties.

4. Conclusion

This paper has summarized experiments using XAS technique to study the quantum confinement properties of EuO-nanocrystals. We have presented the Eu L$_3$-edge XANES spectrum of EuO-nanocrystals. The XANES spectrum shows that the ionization energy of Eu-ions decreases from 6977-eV (bulk EuO) to 6972-eV (EuO-nanocrystals). In this case the red-shift of the ionization energy is present when the size of the crystals is decreased.

The Eu L$_3$-edge XANES spectrum can also be used to describe the primary electron transition of Eu^{2+} between 4f and 5d orbital for bulk EuO.

From the Eu L$_3$-edge XANES spectrum of EuO-nanocrystals, we found that there could be a phenomenon that can refer to the split of the energy band.

The results of the EXAFS technique show that the distances of the inter-atomic of EuO-nanocrystals are decreased.

Finally, we expect that both XANES and EXAFS techniques which include a photoemission technique using synchrotron light will make it possible to characterize the mechanism of the formation of EuO-nanocrystals, so that we are able to improve the quantum confinement model.

5. Acknowledgment

6. Reference

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