Quantum Confinement Properties of EuO Nanocrystal Using Synchrotron Spectroscopy Techniques

Packpoom Sukveeradachgul[1*], Wanchai Pijitrojana[1] and Wantana Klysubun[2]

[1]Department of Electrical Engineering, Faculty of Engineering, Thammasat University, Klong Luang, Pathumthani, 12120, Thailand

[2]National Synchrotron Research Center (NSRC), Nakornrachasima, 30000, Thailand

**Corresponding author. E-mail: spackpoom@gmail.com*

ABSTRACT

Europium Oxide (EuO) has been investigated as a new promising magnetic material for the recording media applications. The quantum confinement structures of EuO nanocrystals are investigated by synchrotron spectroscopy techniques. We study the qualification of nanocrystals on the followings: the physical structure, optical property, electronic band structure and atomic structure of nanocrystals. EuO-nanocrystals have been synthesized by dissolving the Eu-metal in liquid ammonia and oxidizing Eu^{2+}-ions solution with oxygen gas within the absolutely vacuum condition. The powder of sample is identified. The physic structure of nanocrystals is studied using XRD technique. The optical property and electronic band structure are studied using 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 EXAFS technique. The spectra of EXAFS are used to explain the type of center atom, numbers of neighbor atoms and the length between the center atom and neighbor atoms. Both of XANES and EXAFS analyses are the combination signal from XAS spectroscopy technique that conducted by synchrotron light from National Synchrotron Research Center (NSRC).

Key words: Synchrotron light, Europium oxide, EuO, XRD, XAS, XANES, EXAFS

INTRODUCTION

In 1961, EuO is discovered by Matthias et al., (1961). It has a crystallized rock-salt structure; at a room temperature it shows the anti-ferromagnetic property. Depending on the variety of physical properties and applications, the crystals of EuO have completely been studied during the 40 years. In the past, the investigation mainly concentrated on bulk EuO properties, such as optical property and magnetic property. For instance, Ahn et al., (1967) discovered the Faraday Effect phenomenon that occurred when the crystals are excited by external magnetic field.

Also, Kawaguchi et al., (1995) found the magnetic switching property, with Curie temperature of EuO that is 69K. These phenomena lead the crystals of EuO to be recognized as a new magnetic material for development of the recording media industry and as a new electronic devices that are built out of the electromagnetic switching theorem and as a new spintronic applications.

Up to now, we known that the properties of EuO strongly depends on its crystal-size and it leads to many of the new occurrences. When the size of crystals was decreased, for example, the energy band was split, the decreasing of the Curie temperature and the increasing of magnetization when temperature was changing were discovered, etc. We call these phenomena as 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.

To further understand the structure and the binding of metal atoms using the principle of X-ray absorption spectroscopy (XAS). This technique presents a unique method to study the properties of materials. 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 the specific atom and is used to determine the oxidation state of 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. Therefore, in this paper, we report the studies on preparation of the EuO-nanocrystals and the characterization of their properties using the XAS technique.

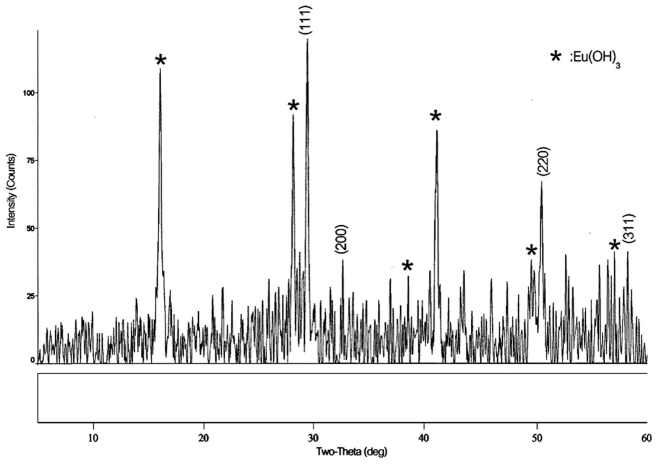


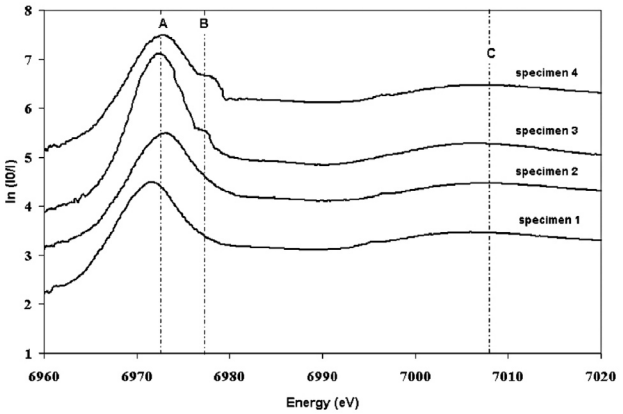
Figure 1. The XRD pattern of EuO-nanocrystals. The peaks at (111), (200), (220), (311) planes identifies the EuO sample.

MATERIALS AND METHODS

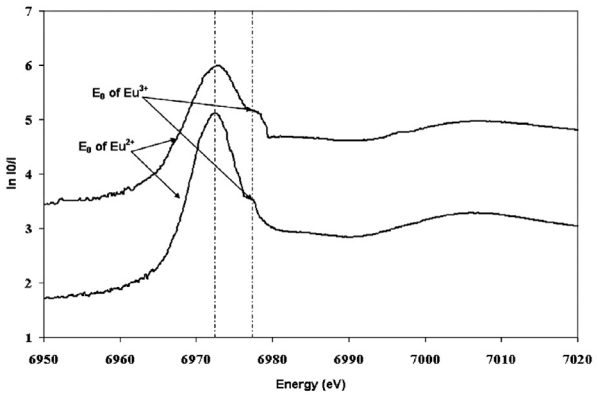
The EuO-nanocrystals were prepared in a nitrogen atmosphere as following: the europium metal (0.5g) was added to liquid ammonia under N_2 atmosphere protecting the solution from the humidity of air. The color of solution becomes strong blue due to the reaction of solvent between an electron of ammonia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

$$\begin{aligned} Eu_{metal} + NH_3 &\rightarrow Eu(II) + 2e^{-}_{ammonia} \\ 2e^{-}_{ammonia} + \tfrac{1}{2} O_2 &\rightarrow O^{2-} + 2NH_3 \\ Eu(II) + O^{2-} &\rightarrow Eu(II)O \end{aligned} \qquad (1)$$

All of processes were freezed with the solid carbon-dioxides 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 excess ammonia. The coarse product was cleaned with HCl (0.1 mol/dm^3) solution, de-ionized water, and methanol, and dried in vacuum to get a grayish white powder product.



(a)



(b)

Figure 2. The XANES spectra of Eu-L_3 edge for EuO-nanocrystals (a) shows the peak energy of absorption atom and (b) shows the inflection point of Eu^{2+} and Eu^{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) according 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. In the other hand, the diffraction peaks are at 2θ = 16.08(2), 27.97(2), 37.45(4), 40.96(2), 49.72(3) and 58.16(5) according to the (100), (110), (111), (201), (300) and (112) planes, respectively, marked with the star symbols (*). They describes the XRD pattern of $Eu(OH)_3$.

In the Eq. (1), the Eu(II)-ions in liquid ammonia being stable at low temperature were dissolved by ammonia-ions until the color of the solution changed to the deep blue color. In liquid ammonia, oxygen gas was reduced into the O^{2-} ions, then they reacted with the Eu(II)-ions that are formed EuO-nanocrystals. However, O^{2-} has the low reaction at low temperature and we knew that the NH3 is separated into NH^-_2 and NH^+_4 in liquid ammonia. So, the reaction of O^{2-} and H^+ might happen and give the OH^- which forms the $Eu(OH)_3$ in the XRD pattern.

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 does not affect to oxygen-ions in the sample.

It is known that the X-ray absorption peaks, so-called white line, appears at the higher energy side of the Eu-L_3 edge energy. The position of white line is responsive to an 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 absorption-ion.

In Fig. 2(a), the XANES spectra have quite complex structures conditioned by contribution of X-ray absorption on europium-ions in 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+}-L3 edge that is located at 6978.58(1)-eV (as shown at peak B). It could be confirmed that there is the 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 the divalent of Eu^{2+} into the trivalent of 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+} that refer to EuO and $Eu(OH)_3$, respectively, which are considered to be the transitions of electron from the $2p_{3/2}$ (O-ions) valence state to the unoccupied-state with 5d-6s (Eu-ions) conduction state above the 4f (Eu-ions) Fermi energy level.

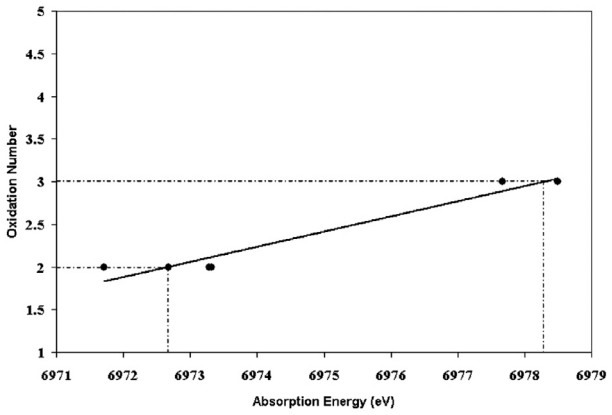


Figure 3. The relation between the oxidation number of Eu-chalcogenides and the absorption edge energy.

Moreover, the XANES spectrum is used to identify the inflection point of the Eu-L3 edge energy that refers to the ionization energy (E0) of Eu-ions. In the Fig. 2(b), the E0 values of Eu^{2+} and Eu^{3+} are 6968.67(7)-eV and 6976.58(5)-eV, respectively. Therefore, the energy of L3 edge of Eu^{2+} is approximated 8.0-eV lower than the L3 edge of Eu^{3+}, so Eu^{2+} ion is ionized easier than Eu^{3+} ion.

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 of absorption edge energy of Eu-chalcogenides. Fig. 3 shows the linearly relation between the oxidation numbers and the edge energy (2003,2006). This graph is use to explain the oxidation number of Eu-chalcogenides at each of the absorption edge energy.

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 consist of two different europium-species that are divalent and trivalent Eu-ions. So, it affected that the structure analysis by EXAFS is not clear and it is not expected to be strong reliable. Therefore, we carried out the structure analyzed for EuO-nanocrystals sample where the dominant valence state of Eu is divalent and we did not concern the comparison of two different europium-species in this paper.

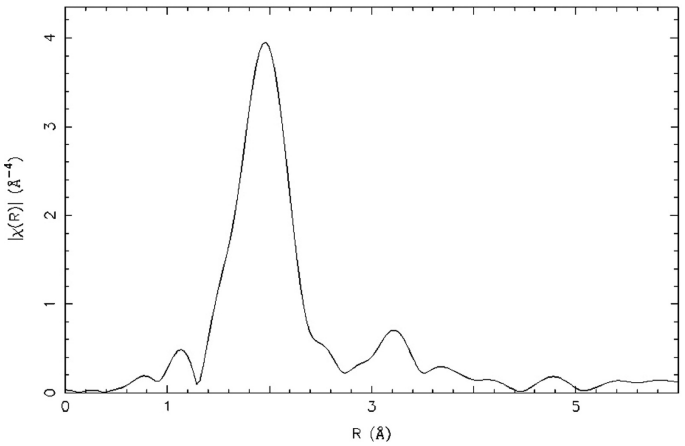


Figure 4. The Fourier transform of k-weighted EXAFS spectra of EuO-nanocrystals.

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. 4. The peak appearing at 2.08(6) $\mathring{A}^{-1}$ is attributed to *Eu* ↔ *O* bond and peak at 3.23(3) $\mathring{A}^{-1}$ is attributed to *Eu* ↔ *Eu* bond. In addition, the peaks, from the inter-atomic distances of 3.67(6) $\mathring{A}^{-1}$ and so on, show the full multiple scattering oscillations of the next neighboring atoms.

Table 1. The summary of EXAFS results from spectra for the EuO-nanocrystals, where R-factor represents the discrepancy index.

Sample	Correlation	Coordination, N	Inter-atomic distance, R (Å)	Debye-Waller factor, σ2 (Å²)	R-factor
EuO	Eu-O	6	2.57(1)	0.044(7)	2.63(3)
	Eu-Eu	12	3.63(7)	0.044(7)	3.69(8)

- Curve-fitting analysis

In order to analyze the details of the measure EXAFS spectra, the curve fitting was carried out using theoretically calculated spectra with IFEFFIT 1.2.9 software (2006). 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 0.5 A, similarly the difference between $Eu \leftrightarrow Eu$ bond obtained from the EXAFS technique and the one obtained from calculation is about 0.42 A. This is due to the size of the crystal decreasing according to the quantum confinement properties.

CONCLUSION

This study has summarized experiments used XAS technique to study the quantum confinement model 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 (nanocrystal EuO). In this case the red-shift of the ionization energy presents when the size of the crystals decreases. 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 nanocrystal, we found that there could be a phenomenon that can refer to the split of the energy band. The results of the EXAFS technique shows the distances of the inter-atomic of EuO nanocrystal are decreased. Finally, we expected that both XANES and EXAFS techniques included 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 and their properties.

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REFERENCES

Ahn, K. Y., and J. C. Suit. 1967. Preparation and properties of EuO films. IEEE Trans Magn. MAG-3(3): 453-455.

Kawaguchi, K., M. Sohma, and Y. Oosawa. 1995. Preparation and magnetic properties of EuO/MgO multilayer film. J. Magn. Magn Mater. 148: 80-82.

Klysubun, W. 2006. Biometry: Experimental technique of x-ray absorption spectroscopy, NSRC.

Matthias, B. T. and R. M. Bozorth. 1961. Ferromanetic Internation in EuO. Phys. Rev. Lett. 7(5): 160-161.

Thongchant, S. 2003. Biometry: Creation of nano-scaled europium (II) compounds as photo-functional materials. Ph.D.Thesis of graduate school of engineering, Osaga University, Japan.