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Mössbauer effect used to study rare-earth oxides synthesized by a high-pressure method

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In the present paper the double rare-earth oxide solid solutions $(\mathrm{Eu}R)\mathrm{O}_3$ ($R=\mathrm{Gd}$, Dy, Ho, Er, Yb, Lu) are synthesized for the first time with a combination of high pressure and high temperature (3.0 GPa and 1080–1250 °C). The analysis of x-ray diffraction shows that all products are *B* type (monoclinic) structures of single phase. Considering $\eta \neq 0$ the ^{151}Eu Mössbauer spectra were fitted by twelve transition lines. It is shown that the isomer shift depends on the unit-cell volume $V^{1/3}$ in a linear fashion.

I. INTRODUCTION

Several double rare-earth oxide solid solutions have been synthesized by the authors in recent years.[1-3] In order to determine their structures and properties, it is necessary to obtain information on double rare-earth valence states. Although the change in a localized region of $4f$ valence electron density in rare-earth solid solution may generally be large, the changes caused by the interaction between two similar rare-earth ions in a well-localized double rare-earth oxide solid solution are small and difficult to detect. Nevertheless, with the high-energy sensitivity of the Mössbauer effect, it is possible to obtain information about the hyperfine interactions.

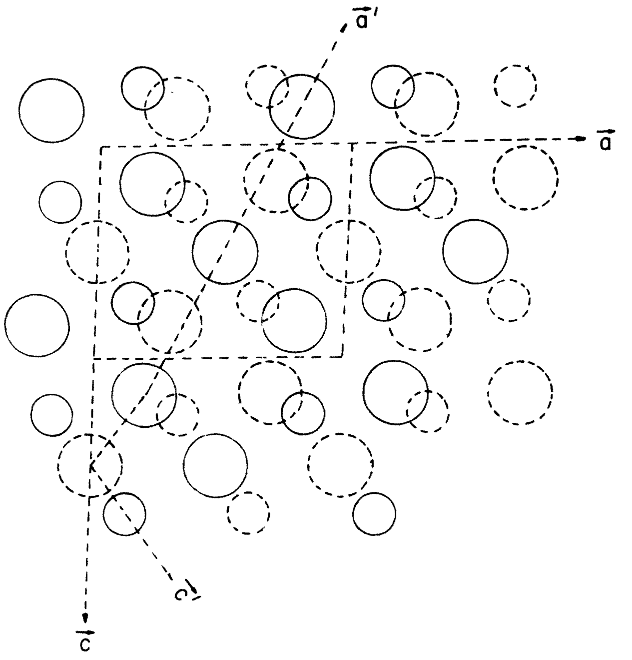

FIG. 1. The projection diagram of the structure of double rare-earth oxide along the [010] direction. The larger circles represent rare-earth atoms, the smaller circles represent oxygen atoms. The solid open circles are in the $\frac{1}{2}$ layer, the dashed open circles are in the 0 layer.

Rare-earth nuclear transitions are complicated, and the hyperfine interactions are very different from those of ^{57}Fe. This brings about some difficulties in fitting rare-earth Mössbauer spectra. So far, little research work on ^{151}Eu Mössbauer effect has been carried out. In the present work, the double rare-earth solid solutions $(\mathrm{Eu}R)\mathrm{O}_3$ with a single phase synthesized with high pressure and temperature were investigated using both x-ray diffraction and the Mössbauer effect.

II. EXPERIMENT

The starting materials used were rare-earth sesquioxides with purities greater than 99.9%. These compounds

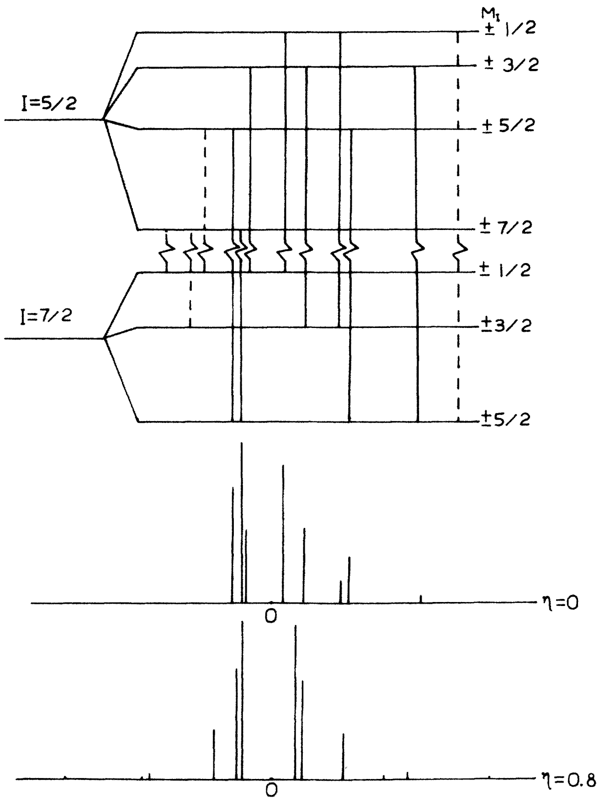

FIG. 2. ^{151}Eu Mössbauer energy level diagram and bar spectrum for $\eta=0$ and $\eta=0.8$.

TABLE I. The lattice parameters of $(\mathrm{Eu}R)\mathrm{O}_3$ solid solutions (±0.004 Å).

Samples	Synthesis condition (3.0 GPa)	a (Å)	b (Å)	c (Å)	v (Å^3)	β (deg)
$(\mathrm{EuGd})\mathrm{O}_3$	1210±10 °C	6.838	3.956	5.963	146.100	93.56
$(\mathrm{EuDy})\mathrm{O}_3$	1190±8 °C	6.794	3.570	5.940	143.783	93.65
$(\mathrm{EuHo})\mathrm{O}_3$	1180±10 °C	6.775	3.549	5.927	142.054	93.70
$(\mathrm{EuEr})\mathrm{O}_3$	1205±5 °C	6.763	3.529	5.928	141.157	93.88
$(\mathrm{EuYb})\mathrm{O}_3$	1230±8 °C	6.733	3.510	5.914	139.446	93.89
$(\mathrm{EuLu})\mathrm{O}_3$	1200±11 °C	6.681	3.519	5.894	138.223	94.06

had bcc structure at room temperature. They were weighed and mixed in equimolar proportion and fired at 950 °C for 30 min. The specimens were then put into sample cells. During the synthesis, a pressure of 3.0 GPa was first applied, and then the temperature was increased to 1080–1250 °C and maintained for 30 min. Then the samples were quenched under pressure, and finally the pressure was released when the samples were cooled to room temperature. After stripping impurities, the samples were ground and the lattice parameters were determined by using x-ray diffraction.

The Mössbauer spectra were recorded with an OXFORD MS-500 spectrometer. The thickness of the absorbers was in the range of 25–40 mg/cm^2. The velocity for the Mössbauer spectrometer was calibrated with a He-Ne laser interferometer. The Mössbauer spectra were fitted using a least-squares method.

III. RESULTS AND DISCUSSIONS

The double rare-earth oxide solid solutions $(\mathrm{Eu}R)\mathrm{O}_3$ were investigated using x-ray diffraction. It was shown that these solid solutions are all of a single phase with B-type structure. The products together with their lattice parameters are tabulated in Table I. The projection diagram of structure of the solid solution is shown in Fig. 1. It can be seen from Table I that the unit-cell volumes gradually decrease with average cation radius.

Since the solid solutions are of B-type (monoclinic) structure, the asymmetry factor for quadrupole splitting is not equal to zero. This complicates the Hamiltonian describing hyperfine interaction. The approximate solution can be obtained only through numerical calculation. In addition, $\eta\neq0$ causes a change from eight to twelve transition lines between the ground state and excited state as is shown in Fig. 2. The relative line positions can be determined by solving the Hamiltonian, and the intensities of resonance lines are obtained from eigenvectors of the Hamiltonian using the multipolarity of the γ ray connecting the two states.[4] According to the expression for the resonance energies and intensities of transition lines, Mössbauer spectra can be fitted with the least-squares method. ^{151}Eu Mössbauer parameters derived from fitting the spectra are listed in Table II. Where δ is the isomer shift, Q_g is the ground-state quadrupole moment. The Mössbauer spectrum of $(\mathrm{EuDy})\mathrm{O}_3$ at room temperature is shown in Fig. 3. The other spectra are similar to that of $(\mathrm{EuDy})\mathrm{O}_3$ and consist of a single, slightly asymmetric, broad line.

It was seen from Table II that there was a definite relation between the atomic number of the second rare-earth element and isomer shift. The relation between isomer shift and unit-cell volume $V^{1/3}$ is shown in Fig. 4.

The following observations can be made from our x-ray diffraction and Mössbauer spectroscopy data for double rare-earth oxide solid solutions $(\mathrm{Eu}R)\mathrm{O}_3$.

(1) Schneider *et al.*[5] have previously synthesized $(\mathrm{Eu}R)\mathrm{O}_3$ using one atmosphere pressure and high tem-

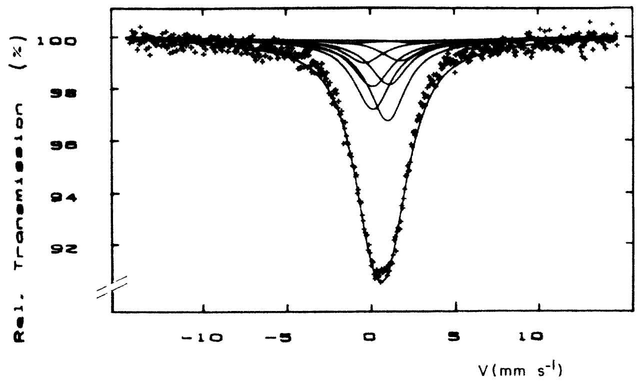

FIG. 3. Mössbauer spectrum of $(\mathrm{EuDy})\mathrm{O}_3$ at room temperature.

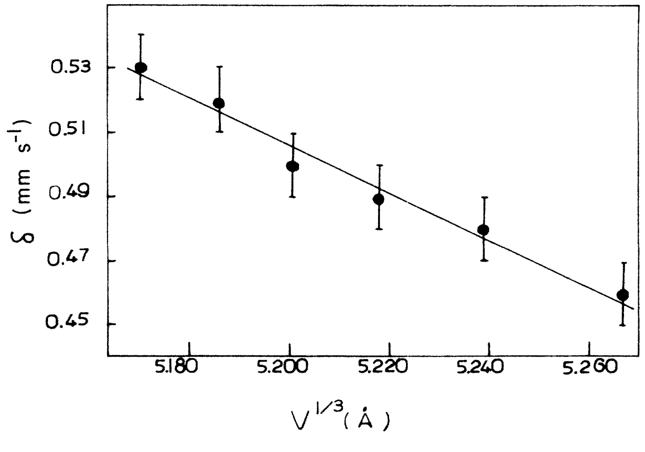

FIG. 4. The relation between isomer shift and unit-cell volume $V^{1/3}$ of double rare-earth oxide.

TABLE II. Mössbauer parameters of $(\mathrm{Eu}R)\mathrm{O}_3$ solid solutions at room temperature.

Samples	δ (mm/s)	$eV_{zz}Q_g$ (mm/s)	η
$(\mathrm{EuGd})\mathrm{O}_3$	0.46 (0.01)	−6.34 (0.23)	0.76 (0.05)
$(\mathrm{EuDy})\mathrm{O}_3$	0.48 (0.01)	−6.41 (0.14)	0.82 (0.03)
$(\mathrm{EuHo})\mathrm{O}_3$	0.49 (0.01)	−7.49 (0.26)	0.88 (0.04)
$(\mathrm{EuEr})\mathrm{O}_3$	0.50 (0.01)	−6.23 (0.28)	0.83 (0.04)
$(\mathrm{EuYb})\mathrm{O}_3$	0.52 (0.01)	−4.98 (0.25)	0.58 (0.08)
$(\mathrm{EuLu})\mathrm{O}_3$	0.53 (0.01)	−6.94 (0.22)	0.81 (0.03)

perature. It was shown that $(\mathrm{EuGd})\mathrm{O}_3$ was of *B*-type structure, $(\mathrm{EuDy})\mathrm{O}_3$ and $(\mathrm{EuHo})\mathrm{O}_3$ were a mixture of solid solutions with *B*-type and *C*-type structures, and $(\mathrm{Eu}R)\mathrm{O}_3$ (R = Er, Yb, and Lu) were of *C*-type structure. We have shown with x-ray diffraction that the solid solutions synthesized using high pressure are all of *B*-type structure, so the $(\mathrm{Eu}R)\mathrm{O}_3$ (R = Er, Yb, and Lu) obtained in the present work are of new phases.

(2) All $^{151}\mathrm{Eu}$ Mössbauer spectra in this work are fitted with twelve lines corresponding to Eu ions in one site. The single line width was fixed on 1.33 mm/s, which is slightly wider than the natural linewidth [1.31 mm/s (Ref. 6)]. The values of χ are less than 1.2, and the theoretical spectra are consistent with the experimental ones. We conclude that Eu atoms are situated in single crystallographic positions of the solid solutions.

(3) Calculations suggest that A and B may be not only trivalent, but also A^{2+} and B^{4+} in many double rare-earth $AB\mathrm{O}_3$ compounds. The isomer shifts for Eu^{2+}-containing compounds are in the range of −11.2 to −13.9 mm/s; the corresponding parameter for Eu^{3+}-containing compounds are in the range of −0.13–1.5 mm/s.[7] Hence, the valence state for the Eu ion can be inferred from the isomer shift. Since the isomer shifts for all samples are in the range of 0.46–0.53 mm/s, Eu ions in the double rare-earth oxide solid solutions investigated in this work are in the trivalent oxidation state.

(4) The following equation can be obtained by fitting the points in Mössbauer spectra with least-squares method:

$$\delta(\mathrm{mm/s}) = 4.393 - 0.745 V^{1/3}\ (\text{Å}) ,$$

where δ is the isomer shift and V is the volume of unit cell.

It is shown that the decreasing of unit-cell volume which is caused by the lanthanide contraction in the second rare-earth elements makes interactions of Eu nucleus with its own s electrons increase. This is a main factor to influence isomer shift. In addition, a part of valence electrons and a little part of $4f$ electrons in the second rare-earth element can either pass through the effective region of $^{151}\mathrm{Eu}$ or interact with oxygen, which results in an increase in the isomer shift.

It is seen from the above that the Mössbauer effect with its high-energy sensitivity can detect small changes in double rare-earth solid solutions $(\mathrm{Eu}R)\mathrm{O}_3$. This provides useful information for understanding the properties of rare-earth solid solutions and compounds.

(5) The quadrupole splitting obtained in this work is negative, indicating that the electric field gradient is also negative and is of the same sign as the lattice contribution. This also shows that the second-order contribution from $4f$ electrons to the electric-field gradient is smaller than the lattice contribution.

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[1] Su Wenhui, Wu Daiming, Li Xiaoyuan, Ma Xianfeng, Zhou Jianshi, Qian Zhengnan, and Wang Yifeng, Physica **139&140B**, 658 (1986).

[2] Su Wenhui, Wu Daiming, Ma Xianfeng, Qian Zhengnan, Wang Yifeng, Li Xiaoyuan, Zhou Jianshi, and Wang Deyong, Physica **139&140B**, 661 (1986).

[3] Su Wenhui and Zhou Jianshi, J. China Rare Earth Soc. (to be published).

[4] K. A. Hardy, D. C. Russell, R. M. Wilenzick, and R. D. Purrington, Nucl. Instrum. Methods **72**, 82 (1970).

[5] S. J. Schneider and R. S. Roth, J. Res. Nat. Bur. Stand. **64A**, 317 (1960).

[6] J. G. Stevens, *Handbook of Spectroscopy*, edited by J. W. Robinson (CRC, Boca Raton, Florida, 1981), Vol. III, p. 464.

[7] G. K. Shenoy and F. E. Wagner, *Mössbauer Isomer Shifts* (North-Holland, Amsterdam, 1978), p. 661.