JOURNAL OF SOLID STATE CHEMISTRY 111, 437–439 (1994)

LETTER TO THE EDITOR

An Energy-Dispersive X-Ray Diffraction Study of Monoclinic Eu_2O_3 under Pressure[1]

G. Chen,* J. R. Peterson,*,† and K. E. Brister‡

*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600; †Transuranium Research Laboratory (Chemical and Analytical Sciences Division), Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6375; and ‡Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14853-8001

Communicated by J. M. Honig, March 9, 1994

The phase behavior of monoclinic (*B*-type) Eu_2O_3 under pressure in a diamond anvil cell was studied at room temperature by energy-dispersive X-ray diffraction at the Cornell High Energy Synchrotron Source. The bulk modulus (B_0) of *B*-type Eu_2O_3, derived from the compression curve obtained, was 140 GPa. A pressure-induced phase transition from the monoclinic to the hexagonal (*A*-type) crystal structure was observed at about 4.7 GPa. The fractional volume change, $\Delta V/V$, under this transition pressure was approximately −2%.

The crystal structures and phase behavior of lanthanide sesquioxides, Ln_2O_3, under various conditions of temperature and pressure have been studied over many years by different research groups (1–5). Recent X-ray diffraction studies of *B*-type Sm_2O_3 and Gd_2O_3 under high pressure directly confirmed that pressure induces a monoclinic (*B*-type) to hexagonal (*A*-type) structural transformation (5a, 5b). However, an important thermodynamic parameter for the $B \rightarrow A$ transition, namely the volume change ΔV, and also the equation of state of *B*-type Ln_2O_3 were not available from these studies, because of the limited resolution of the energy-dispersive X-ray diffraction systems used (5a, 5b). In a recent luminescence study of *B*-type Eu_2O_3 under pressure, we have similarly observed a phase transition from the monoclinic to the hexagonal structure under increasing pressure (5c). We wanted to confirm this previous result based on luminescence spectroscopic analysis by using the more direct X-ray diffraction analysis technique. In addition, our goals in the present work were to quantify the volume change occurring with the pressure-induced $B \rightarrow A$ phase transition and to determine the value of the bulk modulus of *B*-type Eu_2O_3 from the compression data up to the transition pressure.

Europium sesquioxide (exhibiting the cubic (*C*-type) structure), with certified purity of 99.9%, was obtained from Ventron (Beverly, MA). Prior to the compression studies, all samples were cleaned of adsorbed contaminants and water by heating the oxide at 1000°C for 5 hr. *B*-type Eu_2O_3 was prepared from this cleaned Eu_2O_3 by annealing at 1350°C for 2 hr. Raman scattering and X-ray diffraction analysis of the heat-treated powder samples confirmed that they indeed exhibited the *B*-type monoclinic crystal structure.

B-type Eu_2O_3 powder was loaded into a diamond anvil cell (DAC), which is similar to the Merrill and Bassett-type DAC and has been described previously (6). Silicone oil was used as the pressure-transmitting medium, and ruby was used for pressure calibration (7).

Energy-dispersive X-ray powder diffraction analysis of the Eu_2O_3 under pressure was carried out at the B1 station of the Cornell High Energy Synchrotron Source (CHESS) (8). Incident white X rays were collimated to about 70 μm just prior to striking the sample in the aligned DAC. The diffracted X rays passed through double slits (each 500 μm) and were detected by an intrinsic germanium detector at a fixed angle ($\theta = 3.777°$) with respect to the incident beam. The relationship between the energy (E) of the diffracted X rays and the lattice spacings (d) is described by Bragg's law:

$$Ed = hc/2 \sin \theta .$$

The fixed angle was determined by analyzing the diffraction from gold foil under ambient conditions in the same position as the Eu_2O_3 sample was in the DAC (9). The resulting energy · distance (Ed) value was 94.095 ± 0.004 keV · Å.

---

[1] The submitted manuscript has been authored by a contractor of the U.S. Government under Contract DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

0022-4596/94 $6.00

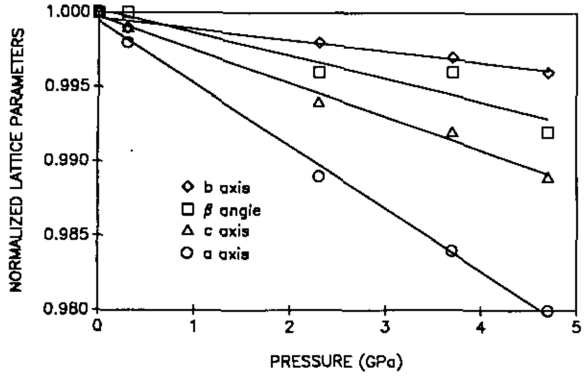

FIG. 1. Normalized lattice parameters $[LP(p)/LP(0)]$ for monoclinic Eu_2O_3 as a function of pressure.

The variations with pressure of the lattice parameters of monoclinic Eu_2O_3 up to 4.7 GPa are illustrated in Fig. 1 by their normalized values (measured value divided by the room pressure value) and are represented by the linear fits

$$a\,(\text{Å}) = 14.108 - 0.060 \cdot P\,\text{GPa}^{-1}$$
$$b\,(\text{Å}) = 3.6018 - 0.002 \cdot P\,\text{GPa}^{-1}$$
$$c\,(\text{Å}) = 8.8073 - 0.019 \cdot P\,\text{GPa}^{-1}$$
$$\beta\,(^\circ) = 100.13 - 0.163 \cdot P\,\text{GPa}^{-1}.$$

From these data the corresponding linear compressibilities are calculated to be

$$\beta_a = 4.25 \times 10^{-3} \cdot \text{GPa}^{-1}$$
$$\beta_b = 5.55 \times 10^{-4} \cdot \text{GPa}^{-1}$$
$$\beta_c = 2.16 \times 10^{-3} \cdot \text{GPa}^{-1}$$
$$\beta_\beta = 1.63 \times 10^{-3} \cdot \text{GPa}^{-1}.$$

The compressibilities along the a and c axes are of the same order of magnitude, whereas that along the b axis is approximately one order of magnitude smaller. This difference in relative compressibilities reveals that the principal structural response to increasing pressure in B-type Eu_2O_3 is compression along the a and c axes, relative to the b axis, in accord with the relative lengths of these lattice dimensions under ambient conditions (amount of axial compression with pressure is directly related to axial length).

The relative volume (V/V_0) data below 4.7 GPa were fitted to the Birch–Murnaghan equation of state:

$$P = \frac{3B_0}{2} \cdot \left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right] \cdot \left\{\frac{1 + 3/4}{4} \cdot (B_0' - 4) \left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}. \quad [1]$$

The bulk modulus (B_0) derived from a one-parameter calculation with the conventional fixed value of 4 for the pressure derivative of the bulk modulus (B_0') is 141 GPa. A least-squares fit of the data based on a two-parameter calculation, in which both B_0 and B_0' are varied, yielded a slightly smaller value of the bulk modulus, 139 GPa, and a larger value, 5.2, for B_0'. Fitting the relative volume (V/V_0) data to the Murnaghan equation,

$$P = [B_0/B_0'][(V_0/V)^{B_0'} - 1], \quad [2]$$

yielded $B_0 = 139$ GPa and $B_0' = 5$.

From analysis of the energy-dispersive X-ray diffraction (EDXRD) data, we found that B-type Eu_2O_3 remained in the monoclinic phase up to 4.7 GPa and then started to transform into a new phase. The diffraction lines from this higher pressure phase can be indexed on the basis of the hexagonal structure known for the A-type lanthanide

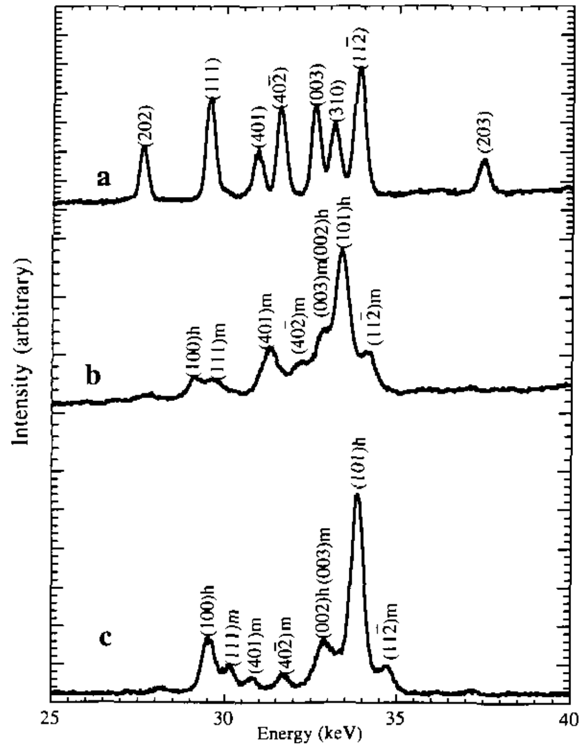

FIG. 2. Energy-dispersive X-ray diffraction patterns from Eu_2O_3 under (a) ambient pressure (all monoclinic), (b) 4.7 GPa (h = hexagonal; m = monoclinic), and (c) 7.2 GPa.

TABLE 1

Miller Indices, Observed and Calculated *d*-Spacings, and Least-Squares Refined Unit Cell Parameters for Monoclinic (*B*-Type) and Hexagonal (*A*-Type) Eu_2O_3 at 4.7 GPa and Room Temperature

h k l			
Monoclinic[a]	Hexagonal[b]	d_{obs} (Å)[c]	d_{calc} (Å)
2 0 2		3.388	3.398
	1 0 0	3.233	3.226
	0 0 2	2.920	2.916
1 1 1		3.175	3.177
4 0 1		3.008	3.008
0 0 3		2.866	2.866
3 1 0	1 0 1	2.819[d]	2.823
3 1 −1		2.761	2.762
6 0 −2		2.159	2.159
3 1 −3		2.118	2.119
	1 1 0	1.862	1.862
	1 0 3	1.664	1.665

[a] *B*-type Eu_2O_3: $a = 13.8224$, $b = 3.5935$, $c = 8.7117$ Å, $\beta = 99.28°$.

[b] *A*-type Eu_2O_3: $a = 3.725$, $c = 5.831$ Å.

[c] $Ed = 94.095 \pm 0.004$ keV · Å.

[d] The relative intensity of this peak is consistent with its being a combination of the 310 line from the monoclinic phase and the 101 line from the hexagonal phase.

sesquioxides and have been reported for the samarium and gadolinium sesquioxides under pressure by Atou *et al.* (5a, 5b). An EDXRD pattern recorded between 20 and 40 keV from *B*-type Eu_2O_3 at 0.3 GPa is shown in Fig. 2a. The EDXRD pattern recorded in the same energy range at 4.7 GPa, which consisted of diffraction from both *B*-type and *A*-type sesquioxide structures, is shown in Fig. 2b. The EDXRD pattern obtained from mixed-phase (with higher content of *A*-type) Eu_2O_3 at 7.2 GPa is given in Fig. 2c. The observed pressure for the *B*- to *A*-type phase transition is 4.7 GPa. All the diffraction peaks recorded at 4.7 and 7.2 GPa can be indexed, based on either the *B*-type monoclinic structure or the *A*-type hexagonal structure. The least-squares refined cell parameters of both crystal structures at 4.7 GPa are listed in Table 1, together with the observed and calculated *d*-values.

From calculations based on the data given in Table 1, the volume change accompanying the $B \rightarrow A$ phase transition, ΔV, is -1.1 Å^3. The fractional volume change, $\Delta V/V$, is about -1.6%. Atou *et al.* have suggested that the mechanism of the pressure-induced $B \rightarrow A$ phase transition in lanthanide sesquioxides may be of a displacive type (5a, 5b). Hyde and Andersson have shown that minor shifts in the oxide ion positions can transform the *B*-type sesquioxide structure into the *A*-type (10). The small volume change accompanying this phase transition provides valuable input to the discussion about the mechanism of this transformation. Because reconstructive-type phase transitions typically give rise to larger discontinuities with pressure in unit cell volume, symmetry, internal energy, etc. than were found here (11), it is likely that this $B \rightarrow A$ phase transition in Eu_2O_3 is of the displacive type.

In summary, the compressibility of *B*-type Eu_2O_3 is anisotropic (greater along the longer *a* and *c* axes). The -1.6% change in the unit cell volume accompanying the $B \rightarrow A$ phase transition in Eu_2O_3 suggests that it is first-order and supports the previously suggested displacive mechanism for it (5a, 5b).

ACKNOWLEDGMENTS

Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Grant DE-FG05-88ER13865 to the University of Tennessee, Knoxville and Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Work conducted at CHESS supported by the National Science Foundation under Award 90-21700.

REFERENCES

1. (a) V. M. Goldschmidt, F. Ulrich, and T. Barth, *Skr. Nor. Vidensk. Akad. Kl. I Mat. Naturvidensk. Kl.*, No. 5 (1925); (b) V. M. Goldschmidt, T. Barth, and G. Lunder, *Skr. Nor. Vidensk. Akad. Kl. I Mat. Naturvidensk. Kl.*, No. 7 (1925).
2. I. Warshaw and R. Roy, *J. Phys. Chem.* **65,** 2048 (1961).
3. R. S. Roth and S. J. Schneider, *J. Res. Natl. Bur. Stand. Sect. A* **64,** 309 (1960).
4. (a) J. O. Sawyer, B. C. Hyde, and L. Eyring, *Inorg. Chem.* **4,** 426 (1965); (b) H. R. Hoekstra, *Inorg. Chem.* **5,** 754 (1966).
5. (a) T. Atou, K. Kusaba, Y. Tsuchida, W. Utsumi, T. Yagi, and Y. Syono, *Mater. Res. Bull.* **24,** 1171 (1989); (b) T. Atou, K. Kusaba, Y. Syono, T. Kikegawa, and H. Iwasaki, *in* "High-Pressure Research in Mineral Physics: Application to Earth and Planetary Science" (M. H. Manghnani and Y. Syono, Eds.), p. 469. American Geophysical Union, Washington, DC (1992); (c) G. Chen, N. A. Stump, R. G. Haire, J. B. Burns, and J. R. Peterson, *High Pressure Res.*, **12,** 83 (1994).
6. J. R. Peterson, U. Benedict, J. P. Young, R. G. Haire, and G. M. Begun, *Microchem. J.* **34,** 76 (1986).
7. H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49,** 3276 (1978).
8. A. L. Ruoff, W. A. Bassett, B. W. Batterman, D. H. Bilderback, and Y. K. Vohra, *Nucl. Instrum. Methods Phys. Res. Sect. A* **266,** 344 (1988).
9. K. E. Brister, Y. K. Vohra, and A. L. Ruoff, *Rev. Sci. Instrum.* **57,** 2560 (1986).
10. B. G. Hyde and S. Andersson, "Inorganic Crystal Structures," Wiley, New York, 1989.
11. C. N. R. Rao and K. J. Rao, "Phase Transitions in Solids," McGraw–Hill, New York, 1978.