# Shock-Induced Phase Transition of $M_2O_3$ ($M$ = Sc, Y, Sm, Gd, and In)-Type Compounds

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Sintered specimens of cubic $Sc_2O_3$-type structure (C-type, $Ia\bar{3}$), $Sc_2O_3$, $Y_2O_3$, $Sm_2O_3$, and $In_2O_3$, and monoclinic $Sm_2O_3$-type structure (B-type, C2/m) $Sm_2O_3$, and powdered specimens of C-type $Gd_2O_3$ were shock-loaded to 2–50 GPa using flyer plates accelerated by a propellant gun. Recovered specimens were studied by X-ray powder diffraction analysis at room and high temperature. $Y_2O_3$ began to transform to the B-type structure above 12 GPa, and the transformation was completed at 20 GPa. $Gd_2O_3$ also transformed to the B-type structure, but residual temperature effects were observed in the yield and crystallinity of the high pressure phase. $In_2O_3$ transformed to the corundum structure ($R\bar{3}c$) in the pressure range of 15–25 GPa, although the yield was very small. Shock-induced phase transition from the C-type to the B-type structure was inferred to proceed via hexagonal $La_2O_3$-type structure (A-type, $P\bar{3}m1$), in comparison with static high pressure experiments.  © 1990 Academic Press, Inc.

## Introduction

The rare earth sesquioxides ($M_2O_3$) are known to exist in three polymorphs despite the similarity in their chemical properties (*1*). Goldschmidt *et al.* denominated them as A, B, and C, and the designations are still in use today (*2*). Their stability at ambient pressure and temperature is understood on the basis of cation and anion radius ratios (*3*). The oxide of larger size cations, $La^{3+}$–$Nd^{3+}$, forms a hexagonal "A-type" structure (space group: $P\bar{3}m1$), which has only one cation site surrounded by seven anions. An intermediate size cation, $Sm^{3+}$ or $Eu^{3+}$, has the "B-type" structure with a monoclinic cell (C2/m), in which cations are in two crystallographically nonequivalent sites coordinated by seven and six anions.

The "C-type" structure, with a cubic cell ($Ia\bar{3}$) in which cations are coordinated by six anions, is found for a whole series of lanthanoid ions as well as the smaller $Y^{3+}$ and $Sc^{3+}$. Since the molar volume of $M_2O_3$ decreases in the transition C → B → A with increasing cation coordination number, high pressure should favor the B- and A-type over the C-type, and the A-type over the B-type. In fact, several compounds of $M_2O_3$ ($M$ = Sc, Y, Ho-Lu) with the C-type structure were found to transform to the B-type structure at high pressure and temperature as recovered by the quenching method (*4–6*). Recently, we observed by *in situ* X-ray diffraction analysis at room temperature that the B-type $Sm_2O_3$ reversibly transformed to the A-type structure under high pressure (*7*). On the other hand, German

*et al.* (*8*) reported in their shock recovery experiments that dynamic compression induced the C–B transformation for several $M_2O_3$ compounds ($M$ = Sm, Dy, Er, Yb, and Y), although detailed information of these transitions was not elucidated yet. The oxides of IIIB group elements having the C-type structure ($In_2O_3$, $Tl_2O_3$) transformed to the corundum structure under static high pressure and high temperature, in contrast to those of IIIA group elements (*9–11*). However, dynamic high pressure experiments of these compounds have not been performed yet.

In the present investigation, the behavior of the rare earth oxides as well as $In_2O_3$ under dynamic high pressure are studied using shock recovery experiments. Complete conversion of the C-type to the B-type structure was observed for $Y_2O_3$ and $Gd_2O_3$, whereas C-type $In_2O_3$ partially transformed to the corundum structure. For the lanthanoids and IIIA group trivalent cations, transition pressures of the C to B were plotted against ionic radius, and we suggest by combining the results of the static high pressure work that the shock-induced "C → B" transitions are intervened with the A-type structure.

**Experimental**

Except for $Gd_2O_3$, starting materials were sintered specimens of reagent grade $Sc_2O_3$ (99.9%), $Y_2O_3$ (99.99%), $Sm_2O_3$ (99.99%), and $In_2O_3$ (99.999%). Each powdered specimen was pressed into a pellet by applying a load of 100 $kgf/cm^2$, sintered at 1700°C for 6 hr in a Keramax electric furnace, and formed into a disk of 10-mm diameter and 1-mm thickness. By X-ray powder diffraction, these oxides were confirmed to have the C-type structure, except for $Sm_2O_3$, which has the B-type structure. Specimens of $Gd_2O_3$ could not be sintered because the C → B transformation occurs at 1200°C at ambient pressure (*1*). Therefore, powder of reagent

grade (99.9%) $Gd_2O_3$ was annealed in air at 700°C for 24 hr to remove water and $CO_2$, and pressed into a pellet of 10-mm diameter and 1-mm thickness. The specimen was confirmed to be a single phase of the C-type structure by X-ray powder diffraction. Bulk density was found to be 90% for $Y_2O_3$ and $Sc_2O_3$, 85% for $In_2O_3$, 98% for $Sm_2O_3$, and 70% for $Gd_2O_3$. To carry out the experiments for different initial density, the sintered specimens were powdered and pelletized into a disk form with a desired density.

The specimen disk was encased in a stainless steel container which was protected from destructive shock effects using a recovery assembly consisting of spall rings and backing plates (*12*). Preheating experiments were carried out by heating the whole recovery assembly using a Ni–Cr heater. For precooling experiments, the whole recovery assembly was cooled by liquid $N_2$. Temperature of the specimen before shot was estimated to be about 100 K.

The impact experiments were carried out using a single stage propellant gun for the pressure range of 2–50 GPa (12). The specimen container was impacted by a flyer plate made of stainless steel, Al2024, teflon or Lexan. Peak pressure was estimated from the measured flyer velocity using the impedance matching method. The shock state in the specimen was considered to be rapidly equilibrated with that of the specimen container via multiple shock reflection between specimen and container interfaces (*12*). Shock duration time was controlled by changing the flyer thickness (3–12 mm).

The recovered specimens were examined by X-ray diffraction analysis using a diffractometer with monochromated $CuK\alpha$ radiation. To estimate an amount of high pressure phase (B-type) semiquantitatively, apparent yield $Y$ is defined as

$$Y = I_B/(I_B + I_C),$$

in which $I_B$ and $I_C$ represent X-ray diffraction intensity of the B-type and the C-type,
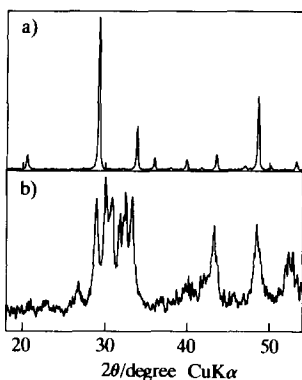
FIG. 1. X-ray diffraction patterns. (a) The C-type $Y_2O_3$ (starting material), (b) the B-type $Y_2O_3$ obtained by shock-loading to 20 GPa.

respectively. $I_B$ and $I_C$ are defined as follows,

$$I_B = I(111) + I(401) + I(40\bar{2}) + I(003) + I(310) + I(11\bar{2}),$$

$$I_C = I(222) + I(400).$$

These diffraction lines were fitted by the Gaussian function to separate them.

Phase stability of the recovered specimens at ambient pressure was examined by high temperature X-ray diffraction analysis, in which the specimens were heated by a Pt heater which served as a specimen plate and temperature was measured by a Pt–Pt/13% Rh thermocouple.

## Results

### $Y_2O_3$

New diffraction lines, other than those of the C-type $Y_2O_3$, were observed in the X-ray diffraction pattern of the specimens shocked above 12 GPa. The diffraction lines of the C-type $Y_2O_3$ completely disappeared in the pressure range of 20–25 GPa, and only new broadened diffraction lines were observed (Fig. 1). These new lines were successfully indexed with the monoclinic cell

of the B-type structure (Table I) with unit cell parameters of $a = 13.88(1)$ Å, $b = 3.513(2)$ Å, $c = 8.629(6)$ Å, and $\beta = 100.09(7)°$. These values are in good agreement with those previously measured (5). The volume decrease of the C $\rightarrow$ B transition was calculated to be 7.2%.

In the diffraction pattern of recovered specimens for pressure above 30 GPa, lines of C-type structure were again observed together with those of the B-type. The amount of the C-type phase increased with increasing pressure (Fig. 2). This phenomenon was explained by the fact that shock-induced residual temperature increased with increasing pressure, resulting in a reverse conversion of the B-type phase to the C-type phase. High temperature X-ray diffraction analysis of the B-type $Y_2O_3$, obtained by shock-load-

TABLE I

Observed and Calculated $d$-Spacings of the B-Type $Y_2O_3$ Obtained by Shock-Loading to 20 GPa

| $h\,k\,l$ | $d_{obs}/A$ | $d_{calc}/A$ | $I$ |
|---|---|---|---|
| 2 0 2 | 3.37 | 3.35 | w |
| 1 1 1 | 3.12 | 3.11 | s |
| 4 0 $\bar{1}$ | 3.00 | 2.99 | s |
| 4 0 $\bar{2}$ | 2.936 | 2.924 | s |
| 0 0 3 | 2.836 | 2.832 | m |
| 3 1 0 | 2.789 | 2.782 | s |
| 1 1 $\bar{2}$ | 2.721 | 2.714 | s |
| 6 0 0 | 2.279 | 2.277 | w |
| 1 1 $\bar{3}$ | 2.228 | 2.225 | w |
| 5 1 $\bar{1}$ | 2.163 | 2.163 | w |
| 3 1 $\bar{3}$ | 2.103 | 2.100 | m |
| 3 1 3 | 1.887 | 1.886 | m |
| 0 2 0 | 1.754 | 1.756 | m |
| 8 0 $\bar{1}$ | 1.734 | 1.734 | w |
| 7 1 $\bar{2}$ | 1.674 | 1.675 | m |
| 4 0 $\bar{5}$ | 1.638 | 1.640 | m |
| 7 1 1 | 1.628 | 1.626 | m |
| 1 1 $\bar{5}$ | 1.547 | 1.547 | w |
| 4 2 1 | 1.514 | 1.515 | m |
| 4 2 $\bar{2}$ | 1.506 | 1.506 | m |
| 8 0 2 | 1.495 | 1.497 | w |

*Note.* $a = 13.88(1)$ Å, $b = 3.513(2)$ Å, $c = 8.629(6)$ Å, $\beta = 100.09(7)°$.
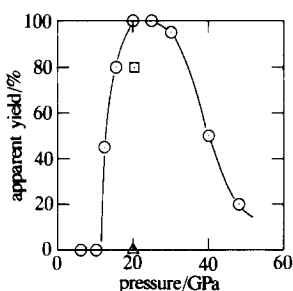
FIG. 2. Apparent yield of the B-type $Y_2O_3$ plotted as a function of pressure. Circle, square, and triangle represent porosity of 10, 30, and 50%, respectively.
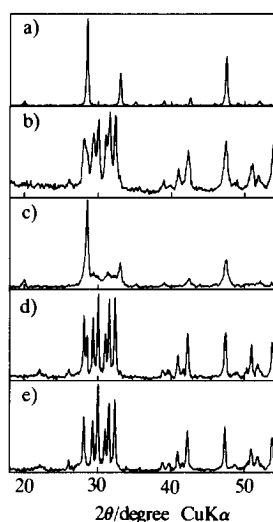


FIG. 3. X-ray diffraction patterns of unshocked and shocked $Gd_2O_3$. (a) Starting material (the C-type structure), (b) shock-loading to 8 GPa, (c) shock-loading to 11 GPa, (d) shock-loading to 14 GPa, (e) shock-loading to 19 GPa.

ing to 20 GPa, shows that the rapid B → C conversion takes place in the range of 400–500°C, though the B-type structure is stable below 400°C. From these observations, the residual temperature is estimated to be below 400°C at 25 GPa.

The effects of the porosity of specimens on the conversion rate were examined at a pressure of 20 GPa. A decrease in initial specimen density caused the decrease in the yield of the B-type $Y_2O_3$, as shown in Fig. 2, in accordance with the increase of residual temperature with decreasing initial density (13).

Preheating shock experiment to 100, 200, and 300°C at 12 GPa resulted in no significant change in the yield of the B-type $Y_2O_3$ compared to normal experiments. This result could be explained if thermal activation is less important to this shock induced C → B transition of $Y_2O_3$ than the pressure effects.

## $Gd_2O_3$

Figure 3 shows the X-ray diffraction patterns of unshocked and shocked $Gd_2O_3$. Diffraction lines of the B-type $Gd_2O_3$ were observed for pressures above 4 GPa, and those of the C-type $Gd_2O_3$ nearly disappeared at a pressure of 8 GPa. Unit cell parameters of the B-type $Gd_2O_3$ obtained by shock-loading

to 8 GPa were determined to be $a = 14.11(1)$ Å, $b = 3.577(2)$ Å, $c = 8.766(3)$ Å, and $\beta = 100.02(5)°$, which were in agreement with those of previous work (14).

The pressure dependence of the yield of the B-type phase was anomalous (Fig. 4). The amount of the B-type phase decreased in the pressure range of 9–13 GPa, but again increased above 14 GPa, and the B-type sin-
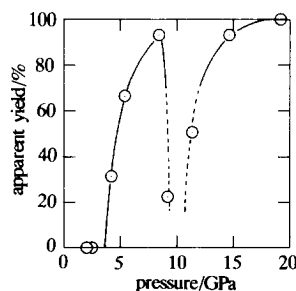


FIG. 4. Apparent yield of the B-type $Gd_2O_3$ plotted as a function of pressure.

gle phase was observed in the pressure range of 20–45 GPa. The diffraction line width of the B-type $Gd_2O_3$ showed marked difference between those obtained above 14 GPa and those obtained below 11 GPa. (Figs. 3b and 3d) The former was much sharper than the latter, indicating that the residual strain in the former was larger than that of the latter.

High temperature X-ray diffraction analysis of the B-type $Gd_2O_3$ obtained by shock-loading to 8 GPa showed that the B-type phase transformed to the C-type phase by heating at 900°C for 2 hr, though the B-type phase was stable to 800°C. The rapid B → C conversion seemed to occur above 1000°C. On the other hand, the C-type $Gd_2O_3$ transformed to the B-type structure above 1200°C at ambient pressure (1). If the residual temperature became 1000–1200°C in the pressure range of 9–13 GPa, the decrease in the yield of the B-type phase in these pressure range could be explained by thermal effects. For pressure above 14 GPa, the B-type structure induced by shock-loading would be maintained, and high temperature would release the residual stress in it. These would make the rate of the B → C conversion small and the quenching of the B-type $Gd_2O_3$ possible.

According to approximate estimates based on the porosity, the residual temperature does not exceed 900°C at 9 GPa and 1200°C at 14 GPa. These were reasonable values for explaining experimental results.

## $Sc_2O_3$

Recovered specimens shocked at 20 and 40 GPa showed very slight broadening of the X-ray diffraction lines compared with the initial C-type materials. There would be two explanations: the C → B phase transition did not occur in this pressure range, or residual temperature caused the reverse conversion from the B-type to the C-type even if the C → B transition had occurred.

## $Sm_2O_3$

Recovered specimens shocked at 30 and 50 GPa maintained the B-type structure of the starting phase, and no appreciable change was observed except for broadening of diffraction lines. If the B-type $Sm_2O_3$ transformed to the A-type within the shock duration time, the A-type $Sm_2O_3$ would revert to the B-type structure after pressure release, because the A-type $Sm_2O_3$ is not stable at ambient pressure, as we reported previously (7).

## $In_2O_3$

In the X-ray diffraction patterns of the specimens recovered from shock-loading at 15 to 25 GPa, new weak diffraction lines other than those of the C-type phase appeared at $2\theta = 22.4°$ and $35.7°$ ($CuK\alpha$). These were identified with the (012) and (110) diffraction lines of $In_2O_3$ with the corundum structure reported by Shannon et al., revealing that the C-type → corundum transition was partially induced by shock-loading (15). Corundum $In_2O_3$ was not observed above a pressure of 30 GPa.

Precooling experiments carried out at 20 GPa showed no appreciable change compared with normal experiments. Low initial density (50%) specimens shocked to 20 GPa showed no corundum phase in both normal and precooling conditions. The variation of shock duration time (1–4 $\mu$s) caused no effect in the yield of the corundum $In_2O_3$. The result of precooling experiments suggests that the small yield of the corundum phase is not caused by a reverse conversion of corundum → C-type due to high residual temperature at ambient pressure, and may be ascribed to slow kinetics of the transition of the C-type to the corundum structure.

## Discussion

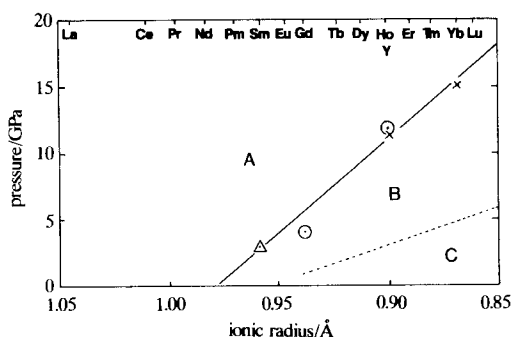The shock-induced C → B phase transition of $Gd_2O_3$ and $Y_2O_3$ was observed above

FIG. 5. The phase transition pressures are plotted against ionic radii of rare earth ions. Circle, C to B transition by shock-loading; triangle, B to A transition by static compression; cross, C to A transition by static compression. Solid line represents "B–A" phase boundary, and broken line represents a virtual "C–B" phase boundary at room temperature.

4 and 12 GPa, respectively. These transition pressures were higher than those known from the static high pressure experiments (4, 5), which were carried out at high temperature (550–1450°C) conditions. If thermal activation is required to induce these phase transitions, temperature achieved in shock compression to this pressure regime would be too low. However, the preheating experiments carried out for $Y_2O_3$ definitely exclude this possibility.

Fujimura et al. reported in their in situ X-ray diffraction experiments that the C-type $Y_2O_3$ and $Yb_2O_3$ transformed to a high pressure phase with the A-type structure at 12 and 15 GPa, respectively, at room temperature in the static condition (16). We also reported that the B-type $Sm_2O_3$ reversibly transformed to the A-type structure at 3 GPa at room temperature (7). In Fig. 5, the transition pressure of the "C to A" or "B to A" transition is plotted against ionic radius (17). A linear relationship between the stabilizing pressure of the A-type phase with respect to the C-type or B-type phase and the cationic radius was clearly seen. Figure 5 also indicates a virtual phase boundary (broken line) between the B-type and the C-type phase at

room temperature which was obtained by extrapolation of the "C–B" phase boundary at 550, 1000, and 1450°C determined by Hoeckstra (5). According to Fig. 5, the stable region of the A-type structure at ambient pressure and temperature is found for $La^{3+}$–$Nd^{3+}$, while cations smaller than $Sm^{3+}$ are stabilized in the B- or C-type structure. These phase stabilities are consistent with those actually known.

The pressure-induced "C–B" transition by shock-loading of $Gd_2O_3$ and $Y_2O_3$ (circle) seems to correspond to the "B–A" phase boundary rather than "C–B" phase boundary. These strongly suggest that the A-type phase intervenes between the shock-induced "C → B" transition. A very short period of shock duration (1 $\mu$s) would prevent the "C to B" transition from occurring. This is consistent with the experimental results of the static "C to A" transition reported by Fujimura et al., in which the B-type phase has not been observed even in the stable region of the B-type phase at room temperature.

If the rate of the "C to A" transition is much higher than that of the "C to B" transition, the former transition would prevail over the latter within shock duration time; hence the A-type structure was realized under high pressure. After pressure is released by rarefaction wave, the A-type phase, which is not stable at ambient pressure except for $La^{3+}$–$Nd^{3+}$, will transform to the B-type structure, which can exist metastably at ambient pressure. Hyde and Anderson showed that the A-type structure resembles very closely the B-type structure and the very small amount of anion shuffling would convert the A-type to the B-type (18). Salem et al. observed the B-type structure, which appeared in epitaxial growth on the A-type crystal on cooling, and interpreted the cooperative A–B transition in terms of the group theory (19, 20). Such "A to B" transition has been also demonstrated in $Sm_2O_3$ at static high pressure (7). From