Structural phase transition in ReO$_3$ under high pressure

Structural phase transition in ReO_3 under high pressure

E Suzuki[1,3]**, Y Kobayashi**[1]**, S Endo**[1] **and T Kikegawa**[2]

[1] Research Centre for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan
[2] Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan

E-mail: esuzuki@hpr.rcem.osaka-u.ac.jp

Abstract
Structural phase transitions in ReO_3 were studied under high pressure with the angle-dispersive x-ray diffraction method using synchrotron radiation. The pressure range of 8–18 GPa was clarified to be the coexistence region of the cubic phase and rhombohedral I phase. In addition, the apparent change of diffraction pattern observed above 38 GPa defined the unit cell of the rhombohedral II phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Many compounds with the perovskite-type structure have been studied because of their variety of properties in solid systems, particularly the structural phase transitions associated with the lattice-dynamical instability. The general formula of the perovskite compound is ABX_3, but the A site is empty in ReO_3. ReO_3 has the cubic perovskite structure ($Pm3m$) at ambient pressure and has a sequence of particular structural phase transitions under high pressure. The emptiness of the A site and the rigidity of the ReO_6 octahedron enable rotation of the ReO_6 octahedron as mentioned below. Thus, it is considered that the rotation of the ReO_6 octahedron induces the majority of the structural phase transitions. Recently, Jøgensen *et al* [1] studied the phase transitions in ReO_3 under high pressure up to 52 GPa with an energy-dispersive x-ray diffraction method (EDX). They reported that the structure changes from the initial cubic $Pm3m$ phase (abbreviated to cubic I, hereafter) to the cubic $Im3$ phase (cubic II) at 0.5 GPa, to the monoclinic MnF_3-related phase at 3 GPa, to the rhombohedral VF_3-related phase (rhombohedral I) at 12 GPa, and finally to another rhombohedral phase (rhombohedral II) at 38 GPa. However, they stated that the indexing of the powder pattern

[3] Author to whom any correspondence should be addressed.
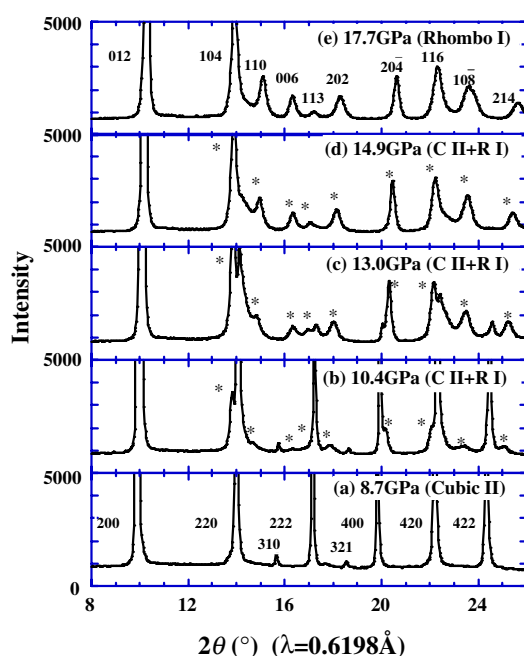
Figure 1. Diffraction patterns of ReO$_3$ obtained in the compression process at room temperature (run I).

obtained to the monoclinic MnF$_3$-related structure was rather difficult because of the limited resolution of the EDX. In addition, they found no appropriate difference between the diffraction patterns of rhombohedral I and rhombohedral II. They concluded this transition to exist from the change in compressibility at 38 GPa. Thus, we have studied the phase transitions in ReO$_3$ under pressure with the angle-dispersive x-ray diffraction method in order to clarify the crystal structures of the high-pressure phases, especially the monoclinic and rhombohedral II phases.

2. Experimental details

X-ray diffraction experiments on a powder sample of ReO$_3$ were performed in a diamond anvil cell (DAC) at room temperature. The sample used in the experiment was obtained from Aldrich Chemical Co. (Catalogue No 38,099-7). The sample and small ruby chips were set together with 4:1 methanol–ethanol mixture as the pressure medium in a hole of a T301 gasket and the pressure was determined with the ruby fluorescence method [2]. Angle-dispersive diffraction was carried out using monochromatized synchrotron radiation ($\lambda = 0.6198$ Å) and an imaging plate detector at BL-18C in the Photon Factory of the Institute of Material Structure Science, KEK.

3. Results and discussion

Diffraction patterns were collected in two runs: run I up to 20 GPa and run II up to 62 GPa. The purpose of run I was the confirmation of the existence of the monoclinic phase and that of run II was the confirmation of the rhombohedral II phase above 38 GPa.

In run I, we observed the change of the diffraction pattern corresponding to the phase transition from cubic II to rhombohedral I. The diffraction peaks of the low intensities obtained
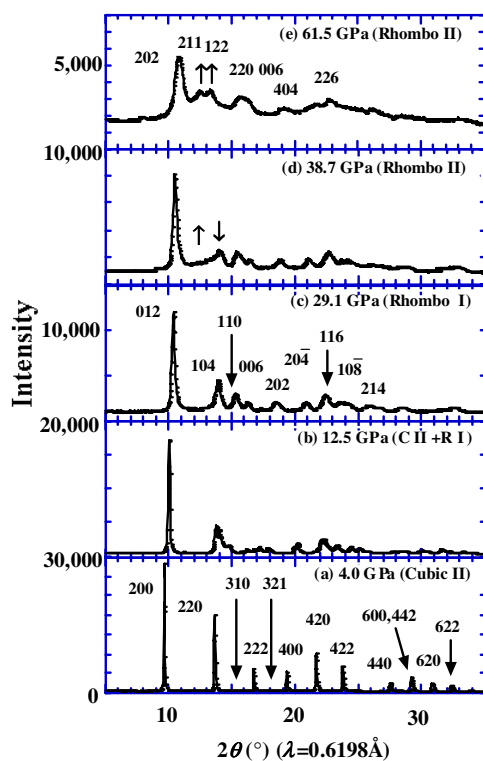
Figure 2. Diffraction patterns of ReO$_3$ obtained in the compression process at room temperature (run II).

in run I are enlarged in figure 1. We have confirmed cubic II phase ($Im3$) by detecting the weak 310 and 321 reflections in the pattern at 8.7 GPa. In the pattern at 10.4 GPa, some new peaks marked with asterisks appeared. With further pressure increase, the intensities of these new peaks increased. On the other hand, the intensities of the peaks for the cubic II phase decreased. The pattern at 17.7 GPa is the same as that of the rhombohedral I phase. The patterns between 8.0 and 18.0 GPa are those of the coexisting cubic II and rhombohedral I phases. Although Jøgensen *et al* reported that the monoclinic MnF$_3$-related phase appeared in the pressure range from 3 to 12 GPa, the diffraction pattern indicating this monoclinic phase was not recognized in the present study and all the patterns obtained were for a mixture of cubic II phase and rhombohedral I phase in this pressure region. In the decompression process, the coexistence region was 3.0–8.0 GPa.

Typical diffraction patterns in run II up to 62 GPa are shown in figure 2. As in run I, we observed three typical patterns below 30 GPa; the pattern of the cubic II phase below 8.0 GPa (figure 2(a)), the coexisting cubic II and rhombohedral I phases between 8.0 and 18.0 GPa (figure 2(b)); and the rhombohedral I phase above 18.0 GPa (figure 2(c)).

With further pressure increase, another change was observed in the diffraction pattern. The appearance of new peaks marked with upward arrowheads in figures 2(d) and (e) and also the disappearance of the 104 reflection (downward arrowheads in figure 2(d)) were observed. This change clarified the occurrence of a new phase transition at about 38 GPa. The patterns between 38 and 62 GPa are almost the same as that of the rhombohedral I phase except the appearance of those two peaks and the disappearance of the 104 peak, considering the
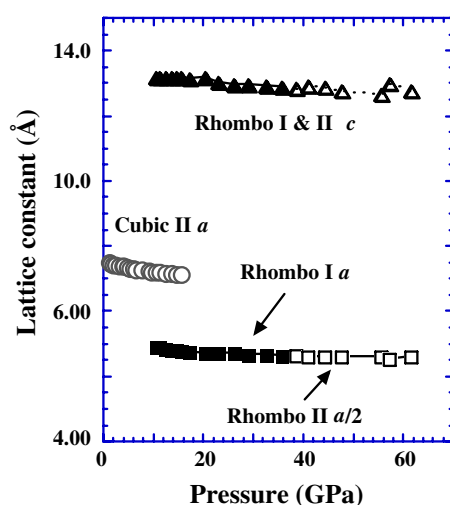
Figure 3. Lattice constants of the three phases of ReO_3 as a function of pressure in the compression process.

Table 1. Zero-pressure bulk modulus (B_0) and zero-pressure volume per chemical formula unit (V_0) for ReO_3.

Phase	B_0 (GPa)	V_0 (Å^3)
Cubic II	40(1)	52.7(1)
Rhombohedral I	63(6)	48.6(4)
Rhombohedral II	190(70)	44(2)

broadening of the peaks. This indicates that the symmetry of this phase is not so different from that of the rhombohedral I phase. We have successfully indexed the diffraction pattern at 62 GPa to a rhombohedral unit cell that is four times larger than that of the rhombohedral I phase—that is, $2a \times 2a \times c$—as shown in figure 2(e). In the decompression process in run II, this rhombohedral II phase transformed back to neither the rhombohedral I phase nor the ambient pressure phase.

The lattice constants of the three phases are shown as a function of pressure in figure 3. The lattice constants a and c of the rhombohedral I phase are continuously related to $a/2$ and c for rhombohedral II phase.

The volume of ReO_3 is plotted as a function of pressure in figure 4. There is a decrease in volume (about 2–3%) at the cubic II–rhombohedral I phase transition, although no appreciable change was observed at the rhombohedral I–rhombohedral II phase transition.

The isothermal bulk modulus B_0 at ambient pressure was calculated using a Birch-type equation of state [3]:

$$P = (3/2)B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}].$$

The values of B_0 obtained for the three phases are listed in table 1. Jøgensen *et al* reported B_0 to be 617(10) GPa for the rhombohedral II phase, which is larger than the value for diamond. But B_0 is 190(70) GPa in the present study. Although the value of the standard deviation is very large for rhombohedral II, our value is definitely different from their value.
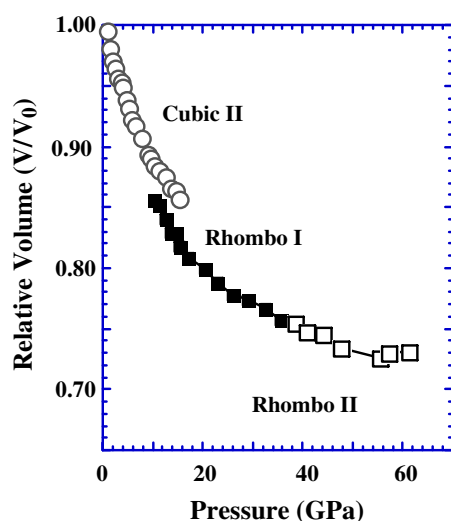
Figure 4. Volume change of ReO_3 as a function of pressure in the compression process. The volume per chemical formula unit at ambient pressure of the cubic I phase (V_0) is 52.62 (Å^3) [4].

4. Conclusions

We have studied the phase transitions in ReO_3 under high pressure with the angle-dispersive x-ray diffraction method. Jøgensen *et al* reported previously that a monoclinic MnF_3-related phase exists in the pressure region from 3 to 12 GPa, but we did not find evidence for this phase. Instead, cubic II and rhombohedral I phases coexist at 8–18 GPa in the compression process and 3–8 GPa in the decompression process.

Furthermore, the change in diffraction pattern was observed above 38 GPa. The diffraction pattern for rhombohedral II was successfully indexed with a rhombohedral unit cell of $2a \times 2\,a \times c$ (a and c are the lattice constants of the rhombohedral I phase). Thus, we have determined the unit cell of the rhombohedral II phase of ReO_3.

Acknowledgment

References

[1] Jøgensen J-E, Olsen J S and Gerwald L 2000 *J. Appl. Crystallogr.* **33** 279
[2] Mao H K, Bell P M, Shaner J W and Steinberg D J 1978 *J. Appl. Phys.* **49** 3276
[3] Birth F 1938 *J. Appl. Phys.* **9** 279
[4] *Powder Diffraction File* JCPDS International Center for Diffraction Data, Swarthmore, PA (Inorganic 33-10968)