

Phase transitions of MgF_2 under high pressure and high temperature

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Introduction

There have been many investigations of post-rutile type structures under high pressure in the field of earth science, crystallography, and solid state physics and chemistry since synthesis of rutile type SiO_2 . Haines *et al.* investigated high-pressure phase transitions of MgF_2 at room temperature as a simple model of the high-pressure behavior of SiO_2 . However, the high-pressure and high-temperature behavior of MgF_2 was not been reported. Recently, we observed the behavior by using an *in-situ* X-ray diffraction method [1]. We introduce the result in this report.

Experimental

X-ray diffraction patterns were collected by an energy-dispersive type method using a large volume cubic press apparatus "MAX80" at PF-AR-NE5C. The detail of high-pressure and high-temperature experiments was described in our article [1].

Result and discussion

Three high-pressure phases were observed in the pressure range up to 15 GPa. Figure 1 shows typical X-ray powder diffraction patterns of MgF_2 , collected by energy-dispersive method. The X-ray diffraction pattern of the ambient-pressure phase with the rutile structure ($P4_2/mnm$, $Z = 2$), as shown in Fig. 1-a, was broadened by increasing pressure under solid state compression at room temperature.

Figure 1-b shows the X-ray diffraction pattern of the high-pressure phase with the CaCl_2 -type structure ($Pnmm$, $Z = 2$) at 11.1 GPa and 27°C, collected after annealing at 500°C.

Some new diffraction lines except for those of the CaCl_2 -type phase emerged by elevating temperature at 13 GPa. All diffraction lines from the CaCl_2 -type phase vanished and the new diffraction lines were only observed at 12.7 GPa and 750°C, as shown in Fig. 1-c. All observed diffraction lines could be indexed on an orthorhombic cell. The indices and relative intensities of the diffraction lines (Fig. 1-c) indicated that the high-pressure phase has the $\alpha\text{-PbO}_2$ type structure ($Pbcn$, $Z = 4$). The $\alpha\text{-PbO}_2$ type phase with a trace of the rutile-type phase was finally recovered at ambient condition. The volume per chemical formula of the $\alpha\text{-PbO}_2$ type phase was 1.1% smaller than that of the rutile-type phase at ambient condition. The bulk modulus of the $\alpha\text{-PbO}_2$ type phase was determined to be $K_0 = 98.0 \pm 0.7$ GPa by fitting the $P - V$ data to the third-order Birch-Murnaghan

equation of state with $K' = 4$. The $\alpha\text{-PbO}_2$ type phase was also confirmed to have a stable region nearby 13 GPa and 600°C.

Another high-pressure phase with the PdF_2 type structure ($Pa-3$, $Z = 4$) was observed at 14.7 GPa and 650°C, as shown in Fig. 1-d.

The present investigation is the first discovery of the stable $\alpha\text{-PbO}_2$ type phase in fluoride compounds. This discovery suggests that high-pressure behavior of difluoride compounds with the rutile structure is similar to that of dioxides and that the stable $\alpha\text{-PbO}_2$ type phase of other difluoride compounds will be found under high pressure and high temperature.

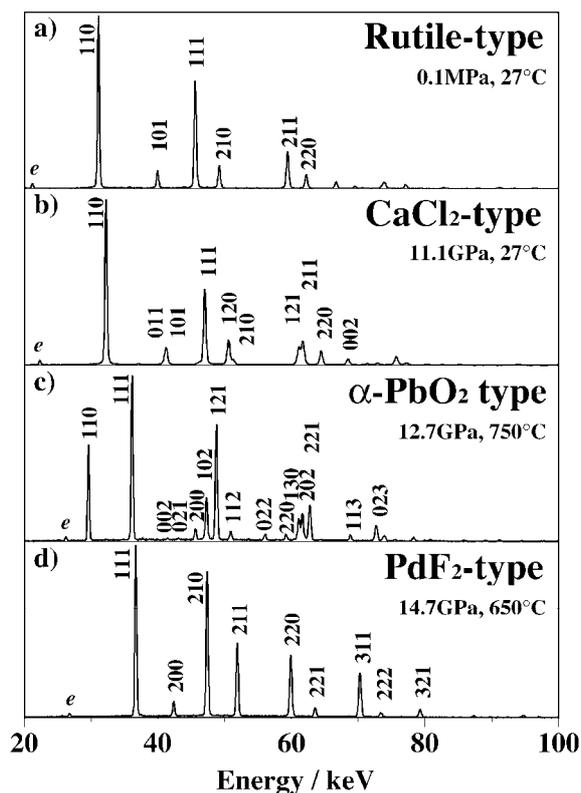


Fig. 1 Typical energy-dispersive type X-ray diffraction patterns of MgF_2 , taken at $2\theta = 6.99^\circ$ [1].

Reference

[1] K. Kusaba *et al.*, Solid State Commun., **148**, 440 (2008).

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