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\(_{2}/\)mmm, 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 (Pnnm, 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 \(\alpha\)-PbO\(_2\) type structure (Pbcn, Z = 4). The \(\alpha\)-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 \(\alpha\)-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 \(\alpha\)-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-\(\bar{3}\), 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 \(\alpha\)-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 \(\alpha\)-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


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