

## Phase transition of $\text{ZnF}_2$ under high pressure and high temperature

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### Introduction

Numerous  $\text{MX}_2$ -type chemical materials with the rutile-type structure ( $P4/mnm$ ) have been investigated about their high-pressure behavior since synthesis of rutile type  $\text{SiO}_2$ . High-pressure behavior of  $\text{ZnF}_2$  was not clear from the viewpoint of crystallography; however it also has the rutile-type structure at ambient condition, as shown in Fig. 1-a). Recently, a pressure-induced transition to the  $\text{CaCl}_2$ -type structure has been observed at 4.5 GPa by a Raman study, and the  $\text{PdF}_2$ -type structure has been predicted to be stable as a high-pressure phase in the pressure condition higher than 6.5 GPa by a theoretical study.

The aim of the present study is to observe high-pressure and high-temperature behavior of  $\text{ZnF}_2$  by high-resolution X-ray diffraction method, and to compare the experimental result with those of the Raman study and the theoretical study.

### 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

X-ray diffraction patterns of  $\text{ZnF}_2$  were broadening by increasing pressure under solid state compression at room temperature. The diffraction pattern became as sharp as that of the starting materials by elevating temperature. All observed diffraction lines at 5.43 GPa and 400 °C could be indexed on an orthorhombic cell of the  $\text{CaCl}_2$ -type structure ( $Pnmm$ ,  $Z = 2$ ), as shown in Fig. 1-b). It was consistent with two previous studies about the rutile- $\text{CaCl}_2$  type transition in  $\text{ZnF}_2$ : the critical pressure value was determined to be 4.5 GPa by the Raman study and to be 4 GPa by the electrical structure calculating study.

Another high-pressure phase observed at 15.3 GPa and 350°C, and all diffraction lines could be indexed on a cubic cell, as shown in Fig. 1-c). The selection rule of the cubic phase ( $0kl$ ;  $k = 2n$  and  $h00$ ;  $h = 2n$ ) demonstrated that the high-pressure phase had the  $\text{PdF}_2$ -type structure ( $Pa-3$ ,  $Z = 4$ ).

The  $\text{PdF}_2$ -type phase remained at room temperature after a cooling process under the high-pressure condition, and the single phase was observed above 4 GPa in a pressure-release process at room temperature. The bulk modulus and initial volume of the  $\text{PdF}_2$ -type phase were

determined to be  $K_0 = 115 \pm 2$  GPa and  $V_0 / Z = 31.99 \pm 0.02 \text{ \AA}^3$ , respectively. These two values were in good agreement with the calculation ( $K_0 = 116$  GPa and  $V_0 = 32.38 \text{ \AA}^3$ ). The determined initial volume of the  $\text{PdF}_2$ -type phase is 8.1 % smaller than that of the rutile-type phase. The X-ray diffraction pattern at ambient condition demonstrated that the  $\text{PdF}_2$ -type phase completely reverted to a mixture of the rutile-type phase and the  $\alpha$ - $\text{PbO}_2$  type phase, as shown in Fig. 1-d).

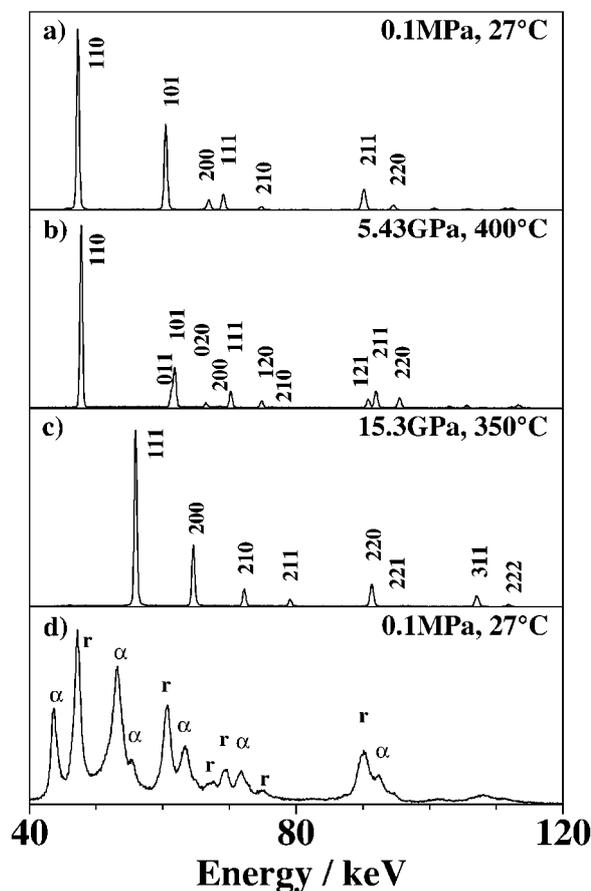


Fig. 1 Typical energy-dispersive type X-ray diffraction patterns of  $\text{ZnF}_2$ , taken at  $2\theta = 4.5^\circ$ ; a) the rutile-type phase, b) the  $\text{CaCl}_2$ -type phase, c) the  $\text{PdF}_2$ -type phase and d) a mixture of the rutile-type phase (r) and the  $\alpha$ - $\text{PbO}_2$  type phase ( $\alpha$ ).

### Reference

[1] K. Kusaba *et al.*, Solid State Commun., **145**, 279 (2008).

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