

## Equation of State Studies on MgF<sub>2</sub> at Room Temperature

상온하에서 MgF<sub>2</sub>에 대한 상태방정식 연구

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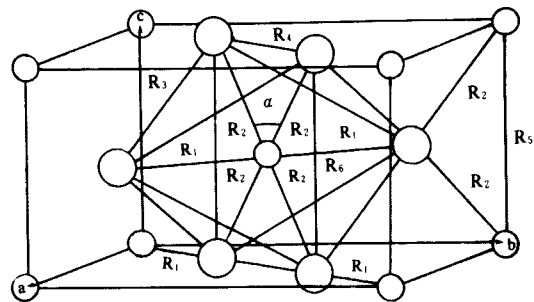
**ABSTRACT:** Polycrystalline MgF<sub>2</sub>(rutile structure) has been studied up to ~15 GPa under truly hydrostatic pressures in a diamond anvil cell(DAC) at room temperature. Its bulk modulus was determined to 96.0 GPa and 97.6 GPa, from two independent runs using Birch-Murnaghan equation of state with an assumed K<sub>0</sub>' of 5.1 from ultrasonic measurements. These are in good agreement with the previously reported values by both ultrasonic and X-ray diffraction methods.

**요약:** MgF<sub>2</sub>(rutile 결정구조) 분말시료를 다이아몬드 앤빌 셀(DAC)을 이용하여, 상온에서 ~15GPa까지 등방 압축실험을 시행하였다. 이 압축실험에 의해 결정된 체적탄성률은 96.0GPa와 97.6GPa였는데, 이는 독립적으로 시행된 두번의 실험결과를 Birch-Murnaghan 상태방정식(K<sub>0</sub>'=5.1로 가정)을 이용하여 결정하였다. 본 실험 결정치는 MgF<sub>2</sub> 단결정을 이용, 초음파법이나 X-선회절 방법으로 측정하여 보고된 값들과 잘 일치하고 있다.

### INTRODUCTION

The rutile structure is commonly observed in dioxides and difluorides at ambient conditions. This tetragonal structure(space group P4<sub>2</sub>/mnm and Z=2) has two cations at (0,0,0) and (1/2, 1/2, 1/2) and four anions at(x, x, 0), (-x, -x, 0), (1/2+x, 1/2-x, 1/2) and (1/2-x, 1/2+x, 1/2). The schematic rutile structure is shown in Fig. 1. The basic unit of this structure is the octahedron of RX<sub>6</sub> where each cation(R)is surrounded by six anions(X). The geometries(i.e., R<sub>i</sub>, i=1,2,3,4,5 in Fig. 1) of each bond in the octahedron are expressed in terms of the lattice parameters, a and c and the anion positional parameter, x.

This crystal structure is geophysically important because stishovite(high pressure polymorph of SiO<sub>2</sub>)with the rutile structure has been considered as one of the major phases in the Earth's mantle(Birth, 1964; Ringwood, 1975). Among the rutile-structured difluorides, MgF<sub>2</sub> is probably most closest to stishovite in terms of ionicity(i.e., of 86%; Rao, 1969)



$$R_1 = \sqrt{2} \times a$$

$$R_2 = \left\{ 2\left(x - \frac{1}{2}\right)^2 a^2 + \frac{1}{4} c^2 \right\}^{\frac{1}{2}}$$

$$R_3 = \left\{ \left(4x^2 - 2x + \frac{1}{2}\right) a^2 + \frac{1}{4} c^2 \right\}^{\frac{1}{2}}$$

$$R_4 = \sqrt{2}(1-2x)a$$

**Fig. 1.** The schematic rutile structure. The large and small circles are anions and cations, respectively. The interatomic distances R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are functions of a, c, and x where x is the positional parameter of anion. R<sub>5</sub> is equal to c. Octahedral angle also is shown between R<sub>2</sub>s.

and the ionic radius ratio of the cation to the anion (i.e., 0.554 of MgF<sub>2</sub>; 0.294 of SiO<sub>2</sub>).

A knowledge of the elastic properties and the high pressure phase transformations of rutile structured analogs can provide valuable information on the behavior of stishovite under mantle conditions (Baur and Khan, 1971). MgF<sub>2</sub> has been extensively studied for its physical and chemical properties from the point of view of high pressure and high temperature phase transformations. The thermal properties at ambient pressure (i.e., 1 bar) (Rao, 1969; Jones, 1977), the elastic properties (Cutler et al., 1968; Bailey et al., 1975; Davies, 1977; Manghnani et al., 1980), high pressure polymorphic studies (Ming and Manghnani, 1979; Ming et al., 1980) and the pressure effect on crystal structure (Baur, 1976; Hazen and Finger, 1981; Nakagiri et al., 1987) of rutile have been studied. The phase transformation pressures in MgF<sub>2</sub> were estimated to be over 25 GPa and 19 GPa at room temperature and high temperature (~1000°C), respectively (Ming and Manghnani, 1979). The high pressure phase has been found to be unquenchable (Kabalkina and Popova, 1964; Ming and Manghnani, 1979).

The stability region of MgF<sub>2</sub> within a wide region of high pressures and high temperatures is the largest among the rutile structured difluorides (see Fig. 3 of Ming et al., 1980). However, based on the relationship between the softening of  $C_s$  (i.e.,  $C_s = (C_{11} - C_{12})/2$ ) and the high pressure phase transformation systematics on rutiles, the transition pressure to a CaCl<sub>2</sub>-type structure in MgF<sub>2</sub> was predicted at ~16 GPa (Ming et al., 1980).

The purposes of this study on MgF<sub>2</sub> are two-fold; (1) to determine the compressibility under truly hydrostatic pressure up to ~15 GPa, and (2) to survey the possible phase transformation at the predicted value.

## EXPERIMENTAL METHOD

### Sample

The polycrystalline specimen of MgF<sub>2</sub> was prepared from the single crystal used for

a previous crystal structural study (Nakagiri et al., 1987) and for the elastic constants measurements using ultrasonic interferometry (Manghnani et al., 1980). The same specimen had been used for high pressure phase transformation studies at both room temperature and high temperature by laser heating (Ming and Manghnani, 1979).

### Experimental Method

The sample and a small circular chip of ruby (~30 μm of diameter) were loaded together in a modified Bassett-type diamond anvil cell (DAC) with a pre-indented Inconel 718 gasket (0.15 mm in thickness Fe-Ni alloy plate with a hole of 0.3 mm in diameter). The pressure medium used to ensure the hydrostaticity was a mixture of 16:3:1, methanol-ethanol-water (Fujishiro et al., 1982) in volume.

The sample pressure was determined by the ruby fluorescence technique (Barnett et al., 1973). For every experimental run, the pressure measuring system was calibrated by the standard ruby at ambient conditions. The pressure of the specimen was measured 5 to 7 times before and after X-ray radiation, respectively. The average values of the R<sub>1</sub> and R<sub>2</sub> peaks were used to calculate the sample pressure. The hydrostaticity in the sample chamber was monitored by the behavior of these two ruby peaks. Broadening of the peaks was taken to indicate the termination of a hydrostatic environment, in the sample chamber then, the experiment was stopped. The uncertainty of pressure determination is estimated to be less than 2%.

Two independent runs have been carried out. In the first run, hydrostaticity was maintained up to ~15 GPa monitoring by the pressure sensor of ruby. However, the second run was terminated at a pressure of ~9 GPa in the load of sample and the pressure medium. In the second run, sample pressures were estimated from the compression data of the first run. There are two reasons for performing the second run; 1) for clearer X-ray diffraction patterns without a ruby chip in the

sample chamber, and 2) for confirmation of the hydrostacity during random pressure loading and unloading processes. Fine focused Zr-filtered MoK $\alpha$  radiation (Enraf-Nonius) of 55 KV and 32 mA was used for these runs. All experiments were conducted at room temperature.

## RESULTS AND DISCUSSION

The d-spacings of the following nine diffraction lines of the sample were measured; (110), (101), (111), (210), (211), (220), (002), (301) and (222). With increasing pressure, the lower intensity lines become obscure. Above ~9 GPa, only four lines, (110), (111), (211) and (301) were used to calculate the lattice parameters. Thus, the accuracy of the determined lattice parameter decreases with pressure from 0.10 to 0.25%.

The lattice parameters, axial ratio and unit cell volumes at various pressures of the two independent runs are listed in Table 1. The lattice parameters a and c, and molar volumes from each run are compared with previously reported values in Table 2.

The compressions of the lattice parameters have been fitted to the following equations;

$$1 - a/a_0 = \Delta a/a_0 = 2.81 \times 10^{-3}P, \text{ GPa (1st run)}$$

and

$$= 2.52 \times 10^{-3}P, \text{ GPa (2nd run)}$$

and

$$1 - c/c_0 = \Delta c/c_0 = 3.04 \times 10^{-3}P, \text{ GPa (1st run)}$$

and

$$= 3.77 \times 10^{-3}P, \text{ GPa (2nd run)}$$

The ratio of a and c can be represented by;

$$c/a = 0.6612 + 3.06 \times 10^{-4}P, \text{ (1st run)}$$

and

$$= 0.6595 - 1.02 \times 10^{-3}P, \text{ (2nd run)}$$

Compression of the a-axis is more consistent than that of the c-axis between the first and the second run. This could be due to the Miller indices used for calculating the c-axis in the rutile structure as discussed by Ming and Manghnani (1979). These two axial compressions are in fairly good agreement with those of Nakagiri et al. (1987). On the

Table 1. The unit cell parameters of MgF<sub>2</sub> under hydrostatic pressures, from two runs

P, Gpa	a*	c*	c/a	V**
0.0001	4.619	3.066	0.6639	65.41
1.25	4.618	3.055	0.6618	65.16
1.93	4.601	3.045	0.6618	64.45
4.80	4.556	3.022	0.6633	62.72
6.10	4.523	3.046	0.6734	62.29
6.69	4.528	2.988	0.6620	61.45
7.61	4.517	3.000	0.6642	61.21
8.43	4.512	2.987	0.6621	60.81
9.02	4.519	2.951	0.6527	60.27
10.12	4.503	2.871	0.6597	60.24
11.25	4.478	2.945	0.6577	59.06
12.30	4.469	2.947	0.6594	58.86
13.16	4.443	2.967	0.6678	58.56
13.81	4.434	2.967	0.6692	58.32
14.85	4.410	2.971	0.6736	57.78
0.0001	4.634	3.052	0.6587	65.54
1.68	4.614	3.028	0.6561	64.46
2.34	4.603	3.023	0.6568	64.05
3.32	4.592	3.013	0.6562	63.53
3.91	4.575	3.020	0.6601	63.21
4.03	4.586	3.000	0.6542	63.09
5.29	4.566	2.995	0.6560	62.44
8.78	4.544	2.947	0.6485	60.85

\* a and c are in units of Å

\*\* V (unit cell volume) is in unit of Å<sup>3</sup>

Table 2. Lattice parameters of MgF<sub>2</sub> at ambient conditions

a*	c*	c/a	V <sub>m</sub> **	References
4.612(1)	3.048(1)	0.6609	19.521	Bailey et al., (1975)
4.6213(1)	3.0519(1)	0.6604	19.625	Baur (1976)
4.628(5)	3.045(3)	0.6580	19.637	Vidal-Valat et al., (1979)
4.631(6)	3.057(4)	0.6601	19.740	Ming and Manghnani, (1979)
4.6233(1)	3.0522(1)	0.66018	19.644	Nakagiri et al., (1987)
4.619(2)	3.066(1)	0.6639	19.696	This study, 1st run
4.634(3)	3.052(2)	0.6587	19.732	This study, 2nd run

\* a and c are in units of Å

\*\* V<sub>m</sub> (molar volume) is in unit of cm<sup>3</sup>/mole

other hand, the *c/a* axial ratios for the two runs contradict each other. Dandekar and Jamieson's *c/a* shows no trend with pressure within their experimental errors (1969). But, *c/a* of Nakagiri et al. increases with pressure. The first run of this study confirms this observation. For the second run, this kind of error might be due to the experimental sequences such as random increase and decrease of pressures in the hydrostatic pressure environment. Regardless of this observation, volume compression is rather well constrained where the effect of pressure is largest on the *a*-axis in the tetragonal system. Regardless of this observation, volume compression is rather well constrained where the effect of pressure is largest on the *a*-axis in the tetragonal system.

The bulk moduli were calculated to be 96.0(23) GPa, and 97.6(2) GPa for first run and second run, respectively. These values were calculated assuming a pressure derivative of 5.1, taken from the ultrasonic value (Manghnani et al., 1980) by fitting the pressure-volume data to the Birch-Murnaghan

equation of state ;

$$P = 3/2 \times K_0 [(V/V_0)^{-7/3} - (V/V_0)^{-5/3}] \times \{1 - \xi [(V/V_0)^{-2/3} - 1]\} \quad (1)$$

where  $V_0$  and  $V$  are the volumes at zero pressure and high pressure, respectively,  $K_0' = (dK/dP)_T$  evaluated at zero pressure, and  $\xi = 3/4(4 - K_0')$ . The first run value shows rather larger uncertainty than the second due to the larger scatter in the data. Despite this, the present values are in good agreement with the previous measurements by ultrasonic and X-ray diffraction methods (Table 3). A comparison of volume compression with the previous studies is shown in Fig. 2.

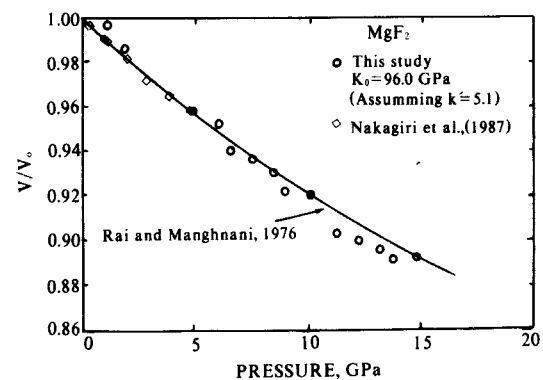
MgF<sub>2</sub> was reported to transform into a cubic "distorted fluorite" structure at ~30 GPa at room temperature (Ming and Manghnani, 1979). Based on a vanishing  $C_s$ , phase transformation pressure of MgF<sub>2</sub> was predicted to be ~16 GPa (Ming et al., 1980). They expected that a high pressure form would be an orthorhombic CaCl<sub>2</sub>-type, and at that pressure, the phase distortion might be too small to distinguish orthorhombic (101) and (011) from tetragonal (101). Their speculation was based on the increase in distortion of the

**Table 3.** Isothermal bulk modulus of MgF<sub>2</sub>

$K_0^*$	$K_0'$	References	Methods & sample**
85.8		Cutler et al., (1968)	US, Sc
100.2		Hausühl (1968)	US, Sc
99.6		Aleksandrov et al., (1969)	US, Sc
106.2		Bailey et al., (1975)	US, Pc
99.6	5.06	Rai and Manghnani, (1976)	US, Sc
102.0	5.1	Davies (1977)	US, Sc
101.1		Jones (1977)	US, Sc
100.6		Kandil et al., (1981)	US, Sc
102.2	5.1	Manghnani et al., (1980)	US, Sc
97.1	5.1	Nakagiri et al., (1987)	XRD, Sc
96.0	5.1	This study, 1st run	XRD, Pc
97.6	5.1	This study, 2nd run	XRD, Pc

\* Isothermal bulk modulus were calculated according to the relation,  $K_s = K_T (1 + \alpha\gamma/T)$ , where  $\alpha$  is volumetric thermal expansivity and  $\gamma$  Grünesien parameter, respectively. \*\* US: ultrasonic method, XRD: X-ray diffraction method. Sc: single crystal, Pc: polycrystalline.

Note:  $K_0'$  of 5.1 for this study was taken from ultrasonic measurements (Manghnani et al., 1980).



**Fig. 2.** Pressure and volume compression data under hydrostatic pressures. Curve shown is from the ultrasonic measurements of Rai and Manghnani (1976). Also shown data from Nakagiri et al. (1987) for comparison.

octahedron unit with increasing pressure, thus elongated differentially in one diagonal direction results in an orthorhombic lattice which slightly deviates from the tetragonal crystal system. Nakagiri et al., (1987) supported this idea pointing out that the octahedral angle variance and mean octahedral elongation indicate the distortion of the octahedron unit increases with pressure in  $\text{MgF}_2$ . Furthermore, they claimed that the point  $(x, c/a)$  moves away from the  $R_1=R_2$  line (see Fig. 5 of Nakagiri et al., 1987), thus the distortion of the octahedron increases in  $\text{MgF}_2$ .

The first run in this study shows that the intensities of several tetragonal diffraction lines, (101), (210), (002), and (222), become weak with increasing pressure, and finally disappear at 9.02 GPa (Fig. 3).

In order to confirm this observation, one more separate run (2nd run) was performed, which turned out the disappearance of those lines at a pressure of  $\sim 8.8$  GPa.

These observations, however, are not enough to clarify the prediction described above, which is based on the extrapolations of the elastic constants (i.e.,  $C_{11}$  and  $C_{12}$  of single crystal of  $\text{MgF}_2$ ) measured at low pressure (i.e., up to  $\sim 1$  GPa) and the statistical fit of  $C_s$

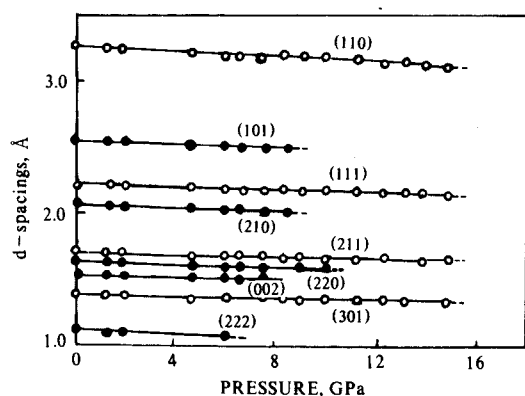


Fig. 3. The variations of  $d$ -spacings with pressures. Empty circles represent the XRD lines which can be observed up to  $\sim 15$  GPa. Solid circles represent the XRD lines which are diminishing intensities with pressure.

in the extended pressure region.

Considering the absorption of X-rays in the diamond itself and the relatively low scattering power of this sample, the reduction of the intensities due to the splitting, or the complete disappearance of these lines can not be ruled out. It is difficult to identify the existence of a transient phase in  $\text{MgF}_2$  by the present film technique. It would be of confidence to verify the well constrained pressure dependence of  $C_s$  to the extended pressures in light of the reported  $K_s$  and/or  $K_T$  values by many investigators with different methods including this study.

## SUMMARY

Polycrystalline  $\text{MgF}_2$  has been compressed under truly hydrostatic pressure conditions in a DAC. Its bulk modulus was determined to be 96.0 GPa and 97.6 GPa, from two independent runs. The zero pressure derivative of the bulk modulus was assumed to be 5.1 which was taken from ultrasonic measurements. These values are in good agreement with the previously reported values by both ultrasonic and X-ray diffraction measurements.

Even though we observe a fade-out of several tetragonal lines with increasing pressure in the X-ray diffracted film, this does not necessarily indicate the complete disappearance and/or the splitting of diffraction lines into those of the  $\text{CaCl}_2$ -type for the predicted transient phase.

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