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HIGH PRESSURE PHASE TRANSFORMATIONS IN MgF_2 (RUTILE)*

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Abstract. Employing a diamond-anvil pressure cell and a YAG laser as a heating source, phase relationships in polycrystalline MgF_2 (rutile) were investigated to ~ 330 kbar at both room temperature ($\sim 23^\circ\text{C}$), and high temperature ($\sim 1300^\circ\text{C}$). *In situ* high pressure X-ray diffraction data show that MgF_2 (I) of rutile structure transforms into MgF_2 (II) of a cubic structure at ~ 300 kbar at room temperature, and at ~ 190 kbar at high temperature ($\sim 1300^\circ\text{C}$), resulting in a negative dP/dT slope for the univariant line between MgF_2 (I) and MgF_2 (II) in the P - T phase diagram. The molar volume differences at room temperature between MgF_2 (I) and MgF_2 (II) at 190 kbar and 300 kbar are $\sim 8\%$ and $\sim 5\%$, respectively.

Introduction

It is generally believed that stishovite (SiO_2 with rutile structure) is one of the most important of the possible constituents in the earth's lower mantle. MgF_2 (rutile), considered as the "weaker" structural analog of SiO_2 (stishovite) [Jones and Liebermann, 1974], has been a subject of several studies in geophysics. Its elastic properties have been determined at ambient conditions [Jones, 1977; Davies, 1977; Aleksandrov et al., 1969; Cutler et al., 1968; Haussühl, 1968], at high pressure [Rai and Manghnani, 1976; Davies, 1977] and temperature [Jones, 1977; Rai and Manghnani, 1976], as well as by theoretical calculations [Striefler and Barsch, 1974]. Its melting curve has been investigated up to 40 kbar [Jackson, 1977]. The phase relations in MgF_2 have been investigated previously by Kabalkina and Popova [1964] up to 140 kbar at 1700°C , and by Dandekar and Jamieson [1969] up to 160 kbar at room temperature. In both of the studies no phase transformation was found. However, on the basis of the theoretically calculated negative pressure dependences of the B_{1g} Raman-active optical mode frequency and $C_s = (C_{11} - C_{12})/2$ shear elastic mode, Striefler and Barsch [1974] predicted the phase transformation pressure for MgF_2 as 97 kbar and 202 kbar, respectively. The objective of the present study was to investigate the phase relations in MgF_2 (rutile) up to ~ 330 kbar at both room temperature ($\sim 23^\circ\text{C}$) and high temperature ($\sim 1300^\circ\text{C}$), using X-ray diffraction techniques involving diamond-anvil pressure cell, and laser heating source.

Sample

The polycrystalline sample of MgF_2 (rutile) was obtained by grinding chips from a single crystal purchased from Optovac, Inc. The lattice parameters of the polycrystalline MgF_2 determined by using a Debye-Scherrer camera (58.76 mm in diameter) are:

$a_0 = 4.631 \pm 0.006 \text{ \AA}$ and $c_0 = 3.057 \pm 0.004 \text{ \AA}$, which are in good agreement with previously reported values ($a_0 = 4.625 \pm 0.002 \text{ \AA}$, $c_0 = 3.052 \pm 0.003 \text{ \AA}$ [Baur, 1956]; $a_0 = 4.6213 \pm 0.0001 \text{ \AA}$, $c_0 = 3.0519 \pm 0.0002 \text{ \AA}$ [Rao et al., 1962]). The molar volume calculated from the present measurements is $19.744 \pm 0.077 \text{ cm}^3/\text{mole}$.

Experimental Method

The pressure cell used in the present study was the Bassett-type diamond-anvil cell [Bassett et al., 1967]. The procedures for loading the sample in the gasket between the diamond anvils, and determination of pressure on the sample by ruby fluorescence technique have been described previously [Ming and Manghnani, 1978a, b]. For the room-temperature runs, sample (powdered MgF_2 + ruby chip) was loaded to desired pressure and X-rayed *in situ* using a fine focus Mo K_α radiation of 50 Kv and 20 mA, and a cassette-type camera with a radius of 50 mm. For high-temperature runs, a small amount of graphite ($<1\%$) was mixed with the powdered sample, and the mixture (powdered MgF_2 + graphite + ruby chip) loaded up to a given pressure and heated to $\sim 1300^\circ\text{C}$ by means of a YAG laser beam with a wavelength of 1.06μ . Sample temperature was estimated from the intensity of the incandescence of the sample, using an optical pyrometer. The laser-heating system and the heating procedure followed are similar to those described in detail elsewhere [Ming and Bassett, 1974]. After quenching the sample from high temperature, sample pressure was measured again. The pressure measured on the post-laser heated samples was generally lower than that on pre-laser heated samples; this is attributed to the flattening of the pressure distribution across the sample during laser-heating [Bassett and Ming, 1972]. The sample pressures reported here are those of the post-laser heated samples.

Experimental Results and Discussion

At room temperature, *in situ* pressure X-ray diffraction data showed that below 270 kbar only MgF_2 (I) of rutile structure was present. As the pressure was increased to 330 kbar, besides the phase MgF_2 (I), a new high-pressure phase MgF_2 (II), as revealed by five new but weak lines (not shown here), was formed. The transformation pressure for the transition MgF_2 (I) $\rightarrow$ MgF_2 (II) was tentatively estimated to be ~ 300 kbar. At ~ 300 kbar, the sample was heated to $\sim 1300^\circ\text{C}$ and then quenched. The pressure on the post-laser heated sample was ~ 250 kbar. The X-ray diffraction pattern of the sample after laser heating and still under pressure (~ 250 kbar) was similar to that obtained at 330 kbar and room temperature except that the intensities of the new lines were enhanced. The d -spacings and intensities for these lines are tabulated in Table 1.

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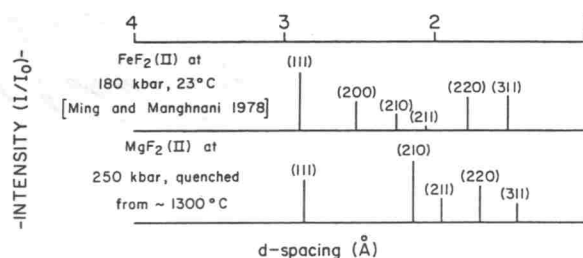


Fig. 1. Comparison of an X-ray diffraction pattern of $\text{MgF}_2(\text{II})$ with that of $\text{FeF}_2(\text{II})$.

Except for two weak lines ($d = 2.407 \text{ \AA}$ and $1.589 \text{ \AA}$), all other lines can be either correlated with the most intense lines (111) and (210) of $\text{MgF}_2(\text{I})$, or indexed by using a cubic unit cell with $a = 4.792 \text{ \AA}$. The d -spacings calculated on the basis of the lattice parameter ($a = 4.792 \text{ \AA}$) are also listed in Table 1 for comparison. The diffraction pattern of $\text{MgF}_2(\text{II})$ is, in general, similar to that of $\text{FeF}_2(\text{II})$ with "distorted fluorite structure" (see Fig. 1), indicating that $\text{MgF}_2(\text{II})$ possesses the same structure as $\text{FeF}_2(\text{II})$. The causes for the diffraction lines of $\text{MgF}_2(\text{II})$ being on the lower d -spacing are the smaller ionic radius of Mg^{+2} (i.e., $0.72 \text{ \AA}$ versus $0.77 \text{ \AA}$ for Fe^{+2}), and the higher *in situ* pressure (i.e., $\sim 250 \text{ kbar}$ versus 180 kbar for $\text{FeF}_2(\text{II})$). The differences in the intensities of the diffraction lines of $\text{MgF}_2(\text{II})$ and $\text{FeF}_2(\text{II})$ may be explained by the differences in the scattering factors for Mg^{+2} and Fe^{+2} .

For investigating the phase relations in MgF_2 at high pressure and high temperature, a series of runs were made at $\sim 1300^\circ\text{C}$ both after loading

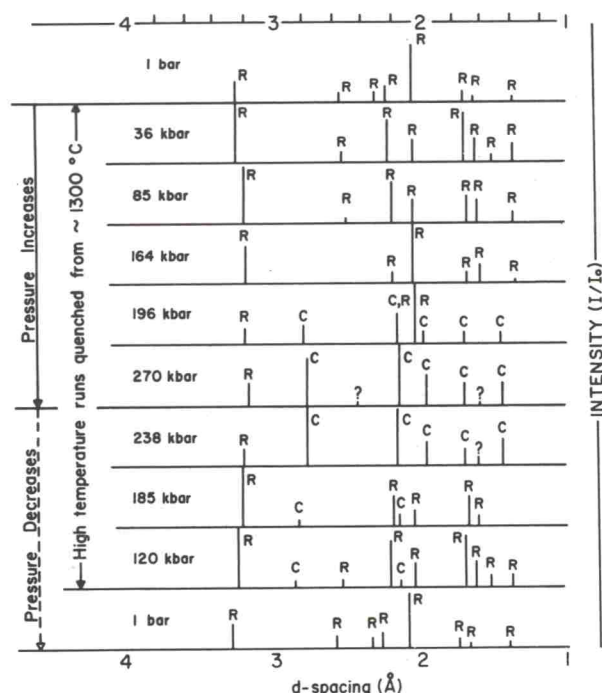


Fig. 2. *In situ* high pressure X-ray diffraction data for MgF_2 (rutile) quenched from 1300°C .

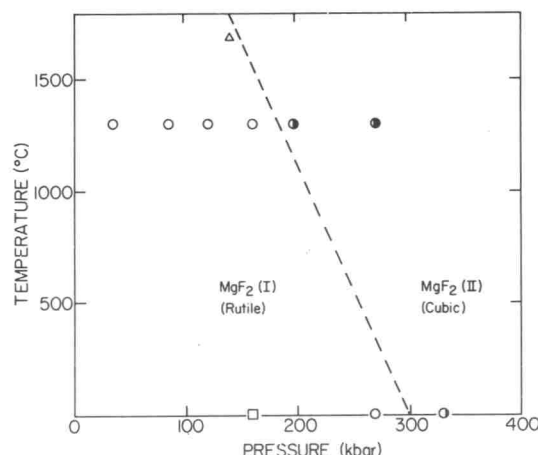


Fig. 3. Pressure-temperature phase diagram for MgF_2 . Notations: $\bigcirc$ and $\bullet$ are the present studies under the loading cycle, representing phase(s) of $\text{MgF}_2(\text{I})$ and $\text{MgF}_2(\text{I}) + \text{MgF}_2(\text{II})$, respectively. Amount of $\text{MgF}_2(\text{II})$ produced is qualitatively proportionate to the black area in the circle. $\square$ from Dandekar and Jamieson [1969], Δ from Kabalkina and Popova [1968].

and unloading processes. *In situ* high pressure X-ray diffraction patterns for the quenched samples (Fig. 2) show that (1) during loading process, transformation of $\text{MgF}_2(\text{I})$ (rutile structure) to $\text{MgF}_2(\text{II})$ ("distorted fluoride structure") starts at $\sim 196 \text{ kbar}$, and is nearly completed at $\sim 270 \text{ kbar}$; (2) during unloading process, most of the phase $\text{MgF}_2(\text{II})$ is transformed back to $\text{MgF}_2(\text{I})$ at $\sim 185 \text{ kbar}$, and a small amount of the phase $\text{MgF}_2(\text{II})$ persists to pressures as low as 120 kbar ; and (3) on releasing the pressure to 1 bar , only $\text{MgF}_2(\text{I})$ of rutile structure is recovered without any metastable phase, such as αPbO_2 , which is usually found, upon unloading, in other rutile-structure compounds; for example, in MnF_2 and ZnF_2 [Kabalkina and Popova, 1964; Dandekar and Jamieson, 1969; Jamieson, 1977], and SnO_2 [Liu, 1978]. Fig. 3 presents the results of the loading runs at both room temperature and those quenched from high temperature, together with the data of Dandekar and Jamieson [1969] and Kabalkina and Popova

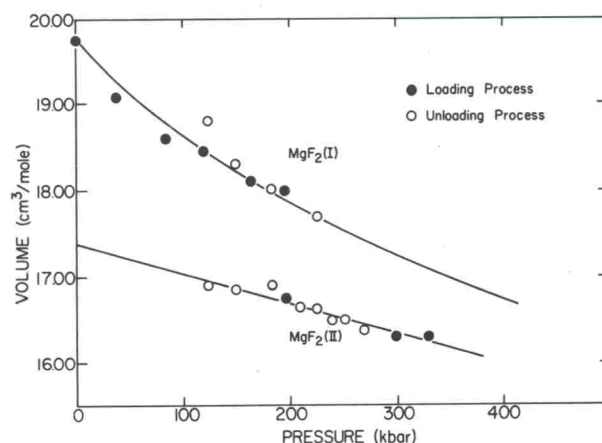


Fig. 4. Pressure-volume relationships for $\text{MgF}_2(\text{I})$ (rutile structure) and $\text{MgF}_2(\text{II})$ (cubic structure) at $\sim 23^\circ\text{C}$.

[1964]. On the basis of the present experimental results, the transformation pressure at $\sim 1300^\circ\text{C}$ for the transition $\text{MgF}_2(\text{I}) \rightarrow \text{MgF}_2(\text{II})$ is estimated to be ~ 190 kbar. Qualitative analysis of all the data gives a negative univariant boundary ($dP/dT \sim -0.086$ kbar/degree) for the transition (Fig. 3). This is not unusual for the rutile-structure difluorides. A negative slope for the same type of phase transformation has also been reported for ZnF_2 [Lityagina et al., 1974]. The pressure dependences of the molar volume of $\text{MgF}_2(\text{I})$ and $\text{MgF}_2(\text{II})$ for the loading and unloading cycles are shown in Fig. 4. The relative molar volume changes for the transition $\text{MgF}_2(\text{I}) \rightarrow \text{MgF}_2(\text{II})$ at the transition pressures at 190 kbar and 300 kbar are estimated to be $\sim 8\%$ and $\sim 5\%$, respectively. This is reasonable in view of the fact that $\text{MgF}_2(\text{I})$ is more compressible than $\text{MgF}_2(\text{II})$ (see Fig. 4). The extrapolated zero-pressure molar volume (V_0) $\text{MgF}_2(\text{II})$ phase is $17.335 \text{ cm}^3/\text{mole}$. The difference in the zero-pressure molar volume of the two phases (ΔV_0) is thus calculated to be $\sim 12\%$, which is comparable to the volume changes found for the same types of phase transformations in other difluorides, e.g., 8% in FeF_2 [Ming and Manghnani, 1978b] and 12% in CoF_2 [Ming and Manghnani, unpublished]. Entropy changes (ΔS) for the transition $\text{MgF}_2(\text{I}) \rightarrow \text{MgF}_2(\text{II})$ at 300 kbar and 190 kbar are evaluated to be ~ 2.0 and ~ 2.6 cal/mole-degree, respectively, using the Clausius-Clapeyron equation.

In view of our findings in other difluorides (e.g., FeF_2 and CoF_2) that the cubic phase further transforms into the hexagonal phase, the

weak and unidentified diffraction lines (see Fig. 2) strongly suggest that $\text{MgF}_2(\text{II})$ should further transform into a denser phase at higher pressures (>400 kbar).

Difluorides with rutile structure have been considered as "weak structure analogs" of dioxides. Their high-pressure phase transformations are, therefore, expected to serve as a model for the rutile-structure dioxides. Recent studies on SnO_2 (rutile) under high pressure (~ 250 kbar) and temperature ($\sim 1000^\circ\text{C}$) [Liu, 1978] show that indeed SnO_2 (rutile) transforms into a cubic phase similar to that found in difluorides [Kabalkina et al., 1969; Ming and Manghnani, 1978; also the present study]. The similar trends in the phase transformation (rutile str. $\rightarrow$ cubic str.) for the rutile-structure difluorides and dioxides greatly enhances the postulate that rutile SiO_2 (stishovite) should transform into a still denser (cubic) phase.

In light of the negative dP/dT slopes for the transition—rutile structure $\rightarrow$ "distorted fluorite structure"—observed in ZnF_2 and MgF_2 [Lityagina et al., 1974, and present study] and for the transition—rutile structure $\rightarrow$ fluorite structure—in ZnF_2 and MnF_2 [Lityagina et al., 1974], it is likely that the boundary between stishovite (SiO_2 with rutile structure) and its denser phase ("distorted fluorite" or fluorite) will also have a negative dP/dT slope. An experimental verification of this postulation will be of great geophysical significance. The larger density increases (~ 8 – 12%) observed for such transformation will then favor the case of mixed oxide phases in the lower mantle, in contrast to the perovskite-structure phases [Jamieson, 1977; Liu, 1978]. Also the negative dP/dT slope, if found in stishovite, would have important implications for geodynamic processes in the earth's deep interior.

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TABLE 1. *In situ* X-ray diffraction data on the lasered sample of MgF_2 which was quenched from temperature of about 1300°C and was still under pressure of ~ 250 kbar

I/I_0	$d_{\text{obs.}} (\text{\AA})$	$\text{MgF}_2(\text{II}),$ rutile str.	$\text{MgF}_2(\text{II}),$ cubic str.	
			(hkl)	$d_{\text{calc}}^* (\text{\AA})$
7	3.182	(111)		
5	2.767		(111)	2.767
<0.5	2.407(?)			
10	2.143		(210)	2.143
2	2.030	(210)		
4	1.955		(211)	1.959
6	1.694		(220)	1.694
<0.5	1.589(?)			
3	1.446		(311)	1.445

$\text{MgF}_2(\text{II})$ = cubic unit cell with $a = 4.792 \text{ \AA}$, $V = 16.569 \text{ cm}^3/\text{mole}$ and $Z = 4$.

* d -spacings calculated on the basis of a cubic unit cell with $a = 4.792 \text{ \AA}$.

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