

An X-ray Diffraction Study on ZrH_2 under High Pressures

고압하에서 ZrH_2 에 대한 X-선 회절 연구

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ABSTRACT : Polycrystalline ZrH_2 in tetragonal crystal system has been compressed in a modified Bassett-type diamond anvil cell up to 36.0GPa at room temperature. X-ray diffraction data did not indicate any phase transitions at the present pressure range. The pressure dependence of the a -axis, c -axis, c/a and molar volume of ZrH_2 was determined at pressures up to 36.0GPa . Assuming the pressure derivative of the bulk modulus (K_0') to be 4.11 from an ultrasonic value on Zr, bulk modulus (K_0) was determined to be 160GPa by fitting the pressure-volume data to the Birch-Murnaghan equation of state. Same sample was heated at 500°C at the pressure of 9.8GPa in a modified Sung-type diamond anvil cell. Unloaded and quenched sample revealed that the original tetragonal structure transforms into a hexagonal structured phase with a zero-pressure molar volume change of $\sim 11.5\%$.

요약 : 결정질 ZrH_2 분말에 대한 압축실험을 바셋-타일 다이아몬드 앤빌기기를 이용하여 상온에서 36.0GPa 까지의 압력 범위에서 시행하였다. 이 시료에 대한 압축실험 결과, 어떠한 상변이도 발견하지 못하였으며, 사방정계에 속하는 ZrH_2 의 격자상수, 축비 및 몰 부피값의 압력에 따른 변화량을 결정하였다. 압력에 대한 체적탄성률의 변화값을 4.11(Zr의 초음파 실험 값)로 가정하였을 때, 버치-머내한 상태방정식을 이용하여 ZrH_2 의 체적탄성률은 160GPa 로 계산하였다. 동일 시료에 대한 고온-고압실험은 성-타일 다이아몬드 앤빌기기를 이용하여 9.8GPa 까지 가압한 후, 약 500°C 로 가열하여 실시하였다. 고온-고압조건에서 상온-상압조건으로 환원한 후, 회수한 시료는 육방정계의 새로운 결정구조로 상변이 하였음이 밝혀졌으며, 이때 몰부피의 변화량은 약 11.5%이다.

INTRODUCTION

Earth's outer core consists of liquid iron alloyed with a small amount of lighter element(s) (Birch, 1964; Brett, 1976; Stevenson, 1981; Brown and McQueen, 1982, 1986). This means that the composition of Earth's outer core is not a pure iron, and contains some amounts of lighter elements than iron itself. Among lots of lighter elements proposed as candidates, hydrogen is one of the possibilities, and only about 1wt% content of hydrogen is enough to explain the density of the

Earth's core (Stevenson, 1981). Recently, a series of studies on iron has been carried out up to the ultra-high pressure conditions for a new fifth phase of iron with the advanced high-pressure technologies (Saxena et al., 1993; Yoo et al., 1995; Saxena et al., 1995).

Geophysically constraining on hydrogen as one of lighter elements of the Earth's core, the behavior of hydrogen in metallic phases is an important knowledge governing the physical properties of a wide range of materials. In this respect, it would be of value to extend for the pressure ef-

fect on the solubility of hydrogen in the metal-hydride phases including iron hydride (Fukizawa, 1982; Fukai, 1992). However, iron hydride in the complete stoichiometry has been proved to be very difficult to synthesize even at high P-T conditions (Badding et al., 1991).

Metal hydrides are one of the possible as well as promising ways for storing hydrogen (Cohen and Wernick, 1981). A full knowledge of its physical, chemical, thermodynamical and crystal structural properties is necessary for its proper use in various applications. Systematic studies of enthalpy and entropy on many metal hydrides have been carried out at ambient conditions (i.e., at both room temperature and atmospheric pressure) (Wiswall, 1978; Cohen and Wernick, 1981). However, it is deficient of experimental data on hydride phases under the extended high pressure and high temperature and/or both conditions. It would be worthwhile that the separate experiments on hydride materials are necessary under the high pressure-high temperature (high P-T) conditions. From this kind of approaches, if any high pressure phases of metal hydrides can be synthesized successfully, they would be one of the useful alternatives for the hydrogen storage because not only it will contain more hydrogen per unit volume but also it will be convenient way to handle as well (Kim, 1992).

On the basis of these views, ZrH₂ was selected after TiH₂ as one of the structural analogs to iron hydride (FeH₂) and for hydrogen solubility into this phase at the extended pressure or pressure-temperature regions (Kim, 1992). Therefore, there are two main purposes of the present research on ZrH₂ under high pressures. The one is the compressional property of this material at room temperature conditions (i.e., the equation of state). The other is to search for any phase transition(s) under pressure with some high temperature conditions.

EXPERIMENTAL METHODS

Sample

Polycrystalline ZrH₂ was prepared in the very fine grain using an agate mortar. This was mixed thoroughly with NaCl powder together at the same ratio in volume. The mixed specimen was examined by angular dispersive X-ray diffraction (ADXRD) technique using both a Debye-Scherrer camera and a high pressure cell. NaCl was used for the geometrical correction of the high pressure XRD camera using its well established *d*-spacings of each XRD line at ambient conditions.

Instrumentation and Experimental Method

A Bassett-type diamond anvil cell (DAC) incorporating a modified anvil rocker assemblage was used in the present study. This DAC consists of two type-I gem-quality diamond anvils (1/3 carat, anvil face 0.5mm in diameter) driven by a piston and screw assemblage. The dimension as well as function of the Bassett-type DAC was described elsewhere (Kim, 1988). An Inconel foil gasket (0.13mm in thickness) with a hole about 0.25 mm in diameter was placed between two diamond anvils so that the hole was centrally located between upper and lower anvils. The fine powder sample was placed into the gasket hole and a small ruby chip approximately 30 μ m in diameter was placed at the center of the hole chamber. The assemblage was then compressed to a desired pressure step-wise. For the runs under hydrostatic conditions (i.e., wet conditions), a mixture of methanol-ethanol-water (MEW) was put into a gasket hole using a plunger before squeezing the DAC. The proportion of MEW each other was 16-3-1 in volume, respectively (Fujishiro et al., 1980). For the non-hydrostatic runs (i.e., dry conditions), none of any pressure medium was used.

Pressure has been determined by the ruby fluorescence calibration method (Barnett et al., 1973). A tiny chip of ruby was situated at the center of the sample chamber, and with increase of pressure the shift of the fluorescence peak of ruby has been converted into pressure values using its well known equation of state. Sample

pressure has been determined by averaging the pressure values before and after X-radiations. The pressure uncertainty thus determined for each run was approximately $\pm 0.06 \text{ GPa}$. Sample was squeezed up to 36.0 GPa at dry conditions and 17.6 GPa at wet conditions, respectively.

At each increment of pressure, the compressed sample in DAC was X-rayed *in-situ* using Zr-filtered microfocused Mo- K_α radiation ($0.1 \times 1.0 \text{ mm}^2$) at 50 kV and 20 mA . The exposure time to X-radiation increases slightly with pressure by virtue of the getting sample mass thinned, and the radiation duration was approximately 70 hours.

For high P-T experiment, a modified Sung-type DAC was used, and the experimental details are described elsewhere (Kim, 1992). The gasket used was 718 Inconel metal alloy with a hole of 0.30 mm in diameter and 0.25 mm in thickness. At first, pressure was increased and then temperature increased up to 500°C using microheater by electric power supply. At this high P-T conditions, sample was sustained for an hour. After quenching and unloading to the ambient conditions, the sample was examined in a Debye-Scherrer camera using Ni-filtered Cu- K_α radiation ($0.1 \times 1.0 \text{ mm}^2$) at 40 kV and 5 mA for ~ 100 hours. Photographic films exposed by X-radiation were read on the film measuring device.

RESULTS AND DISCUSSIONS

Compression at Room Temperature

Polycrystalline ZrH_2 was gradually loaded in a dry conditions up to 36.0 GPa as well as in a wet conditions up to 17.6 GPa . The reason to stop increasing pressure at wet conditions is that MEW transforms into the solid phase above $\sim 18 \text{ GPa}$ (Fujishiro et al., 1980). No phase transitions were observed at both pressure conditions within the present pressure ranges. The d -spacings of five to eight diffraction lines such as (101), (110), (002), (200), (112), (211), (202), (220) of ZrH_2 were observed at lower pressures regions, but only 4 dif-

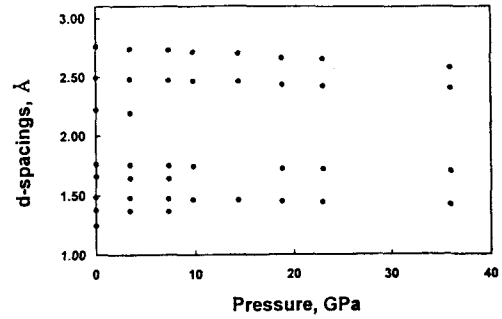


Fig. 1. The effect of pressure on the interplanar d -spacings of the tetragonal ZrH_2 at room temperature and a dry conditions. The corresponding Miller indices for each of the d -spacings are (101), (110), (002), (200), (112), (211), (202), (220) from the top.

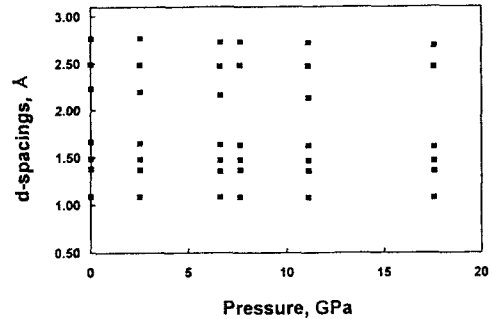


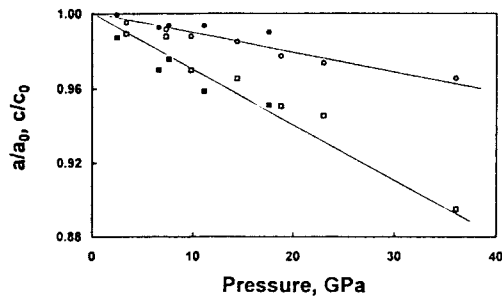
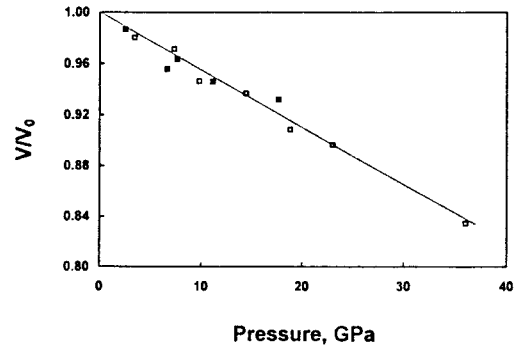
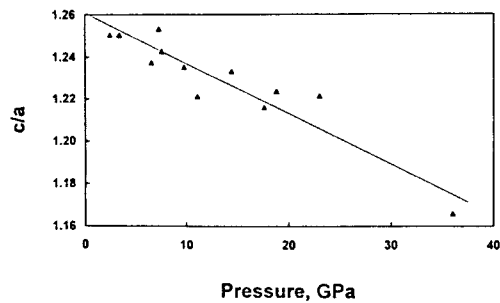
Fig. 2. The effect of pressure on the interplanar d -spacings of the tetragonal ZrH_2 at room temperature and a wet conditions where the corresponding Miller indices for each of the d -spacings are (101), (110), (002), (200), (112), (211) and (301) from the top.

fraction lines of (101), (110), (200) and (211) were measurable above 15 GPa at dry conditions. This fact is expected because sample is getting thinner with increasing pressure and thus the weak lines observed at low pressures would have intensity too weak to be detected at higher pressures. In wet conditions, however, (301) XRD line was observed instead of (202) and (220) and 6 XRD lines except (002) sustain up to 17.6 GPa . The compression patterns of d -spacings with pressure at both dry and wet conditions are shown in Figs. 1 and 2, respectively.

Table 1. The effect of pressure on the lattice parameters(a , c), the axial ratio(c/a) and the volume of the tetragonal ZrH_2 at room temperature

Pressure, GPa	a/a_0	c/a_0	c/a	V/V_0	Remarks*
3.4	0.9953	0.9893	1.2503	0.9802	d
7.3	0.9916	0.9878	1.2532	0.9713	d
9.8	0.9879	0.9699	1.2351	0.9465	d
14.4	0.9850	0.9655	1.2332	0.9368	d
18.8	0.9775	0.9507	1.2235	0.9085	d
23.0	0.9738	0.9454	1.2213	0.8965	d
36.0	0.9656	0.8949	1.2658	0.8344	d
2.5	0.9995	0.9874	1.2504	0.9864	w
6.6	0.9926	0.9702	1.2373	0.9558	w
7.6	0.9938	0.9757	1.2427	0.9637	w
11.1	0.9936	0.9587	1.2213	0.9465	w
17.6	0.9901	0.9511	1.2160	0.9323	w

*d: dry conditions, w: wet conditions


Fig. 3. The effect of pressure on the lattice parameters, a and c of ZrH_2 at room temperature conditions. Circles are for a/a_0 and squares for c/a_0 . Solid symbols for both are from wet conditions.

Fig. 5. The compression of volume, V/V_0 of ZrH_2 . Solid symbols are from wet conditions.

Fig. 4. The effect of pressure on c/a of ZrH_2 . Solid symbols are from wet conditions.

On the basis of the d -spacings measured at various pressures, lattice parameters and the ratio of a/a_0 , c/a_0 , c/a and V/V_0 were obtained. Results of these compression data are shown in Table 1 and Figs. 3, 4 and 5, respectively. Lattice parameter of ZrH_2 at ambient conditions was determined to be $a_0=3.500\text{\AA}$ and $c_0=4.470\text{\AA}$. The compression of the lattice parameters can be represented by: $1 - a/a_0 = \Delta a/a_0 = 1 - 9.8 \times 10^{-3}P(\text{GPa})$ and $1 - c/a_0 = \Delta c/a_0 = 1 - 27.9 \times 10^{-3}P(\text{GPa})$. These quantitative results show that the compression along c -axis is higher than that along the a -axis by approximately a factor of three. The change of c/a with pres-

sure can be represented by $c/a=1.262-24.3 \times 10^{-3} P$ (GPa). The axial ratio of c/a decreases with increasing pressure.

Isothermal bulk modulus at zero pressure (K_0) can be determined by means of the least squares fit of the present experimental data of V/V_0 to the Birch-Murnaghan equation of state :

$$P = \frac{3}{2} K_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \cdot \left\{ 1 - \xi \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\} \quad (1)$$

where V_0 and V are the molar volume at zero pressure and at pressure P , respectively, $K_0' = (dK/dP)_T$ evaluated at $P=0$ and $\xi=3/4 \cdot (4-K_0')$. Since the present X-ray data are not sufficiently accurate to permit an unambiguous determination of K_0' and K_0 for (1), we have assumed the value of K_0' to be 4.11 from ultrasonic measurement on the pure Zr metal (Fisher and Manghani, 1971) and have calculated K_0 from (1) to be 160 ± 5 GPa, where the uncertainty consists of errors from both V/V_0 and pressure determinations. This value is much higher than that of pure Zr (i. e., $K_0=95$ GPa) implying that the nature of the bonding in ZrH_2 is quite different from that in the pure Zr metal of hexagonal crystal system (i. e., $a_0=3.226$, $c_0=5.146$, $V_0=13.97$ cm³/mole). Similar results were also observed in both $VH_{0.5}$ and $NbH_{0.75}$ with respect to their pure metal phases (Fukizawa, 1982).

A tentative comparison with TiH_2 (see Table 1 of Kim, 1992) shows that ZrH_2 is more compressible than TiH_2 . However, K_0 of iron hydride ($FeH_{0.9}$) has been determined to be 121 GPa in the presence of both excess hydrogen and excess iron (Badding et al., 1991). This iron hydride is not in complete stoichiometry and is assigned as the double hexagonal close-packed crystal structure with interstitial hydrogens at octahedral sites. It is hardly to identify the systematics based on the bulk modulus of these hydrides at this moment.

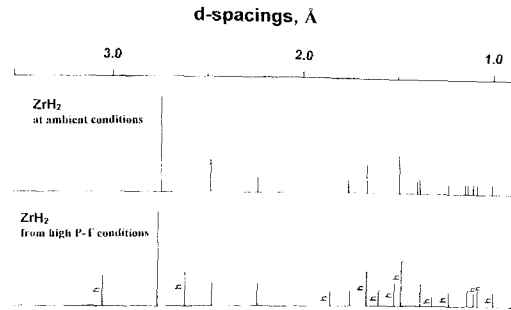


Fig. 6. A schematic diagram for the XRD patterns of ZrH_2 at ambient conditions and that unloaded and quenched from 9.8 GPa and 500 °C, respectively where h is for hexagonal phase. The untransformed tetragonal XRD lines at 9.8 GPa and 500 °C conditions correlate with those of the starting phase consequently.

Experiments at High Pressure-Temperature Conditions

Polycrystalline sample of ZrH_2 was loaded to 9.8 GPa and heated to ~ 500 °C for 60 minutes in the modified Sung-type DAC. XRD data shows that besides the diffraction lines from the starting tetragonal phase, there are 6 new lines indicating a new polymorph of ZrH_2 (Fig. 6). These new XRD lines could be explained on the basis of a hexagonal crystal system unit cell with $a=5.252$ Å and $c=6.090$ Å. Table 2 shows a fairly good agreement between the observed and the calculated d -spacings for a hexagonal phase. If the number of formula per unit cell (Z) is assumed to be 6, then the zero-pressure molar volume is 14.60 cm³/mole, which is $\sim 11.5\%$ smaller than that of the tetragonal phase (i. e., 16.49 cm³/mole).

It is worth noting that the lattice parameters and the axial ratio (i. e., $c/a=1.16$) for a hexagonal ZrH_2 are closely related to those found in the ω -Zr (i. e., $a=5.035$ Å, $c=3.141$ Å, $c/a=0.62$, $V_m=14.60$ cm³/mole) (Ming et al., 1981). The ω -Zr is a simple hexagonal structure with $Z=3$ and is a high pressure phase stable only at

Table 2. X-ray diffraction data of ZrH₂ quenched and unloaded from 500°C and 9.8GPa, respectively

<i>I</i> / <i>I</i> ₀ (obs.)	<i>d</i> (obs.), Å	Tetragonal phase*		Hexagonal phase**	
		<i>d</i> (cal.), Å	(<i>hkl</i>)	<i>d</i> (cal.), Å	(<i>hkl</i>)
30	3.046			3.045	(002)
100	2.756	2.755	(101)		
35	2.612			2.626	(110)
20	2.471	2.475	(110)		
33	2.232	2.235	(002)		
15	1.850			1.854	(103)
15	1.748	1.750	(200)		
35	1.660	1.659	(112)	1.654	(211)
15	1.594			1.606	(113)
20	1.512			1.516	(300)
				1.514	(203)
45	1.476	1.477	(211)	1.471	(301)
20	1.376	1.377	(103)		
		1.378	(202)		
10	1.313			1.313	(220)
				1.312	(213)
12	1.230	1.237	(220)	1.235	(311)
15	1.129	1.134	(203)		
		1.129	(301)		
15	1.104	1.106	(310)	1.102	(223)
10	1.078	1.079	(213)	1.071	(313)
		1.074	(311)		
10	0.992	0.992	(312)	0.987	(322)

* Tetragonal phase, $a=3.500\text{Å}$, $c=4.470\text{Å}$, $c/a=1.277$, $V_m=16.491\text{cm}^3/\text{mole}$, $Z=2$

** Hexagonal phase, $a=5.252\text{Å}$, $c=6.090\text{Å}$, $c/a=1.159$, $V_m=14.60\text{cm}^3/\text{mole}$, $Z=6$

pressures higher than $\sim 2\text{GPa}$ at room temperature (Jamieson, 1963; Vohra, 1978; Ming et al., 1981). The structural relationships existing between high pressure phase of ZrH₂ and that of Zr such that $a_0(\text{ZrH}_2\text{-II}) \doteq a_0(\omega\text{-Zr})$ and $c_0(\text{ZrH}_2\text{-II}) \doteq 2c_0(\omega\text{-Zr})$ seem to suggest that high pressure phase of the hexagonal ZrH₂ is a ω -Zr related phase.

In a similar study on TiH₂, the starting tetragonal phase transforms into orthorhombic crystal system with reduction of volume at $\sim 10\%$ (Kim, 1992). The volume change rate at both materials does not differ much, but their high P-T products belong to the independent crystal systems. In a view of iron hydride in hexagonal system at am-

bient conditions, others are in tetragonal system so that their diverse high P-T products are acceptable and needed more works on the metal hydrides systematically.

SUMMARY

The XRD experimental results on ZrH₂ under high pressures at room temperature as well as from heat-treated at high pressure are summarized as follows :

(1) ZrH₂ in tetragonal crystal structure is much less compressible than the pure metal Zr.

(2) The compression along c-axis is higher than that along a-axis by approximately a factor

of 3, resulting that the axial ratio of c/a decreases with increasing pressure.

(3) Assuming the value of K_0' to be 4.11 of pure Zr metal, bulk modulus has been calculated to be $160 \pm 5 GPa$ using the Birch-Murghnan equation of state.

(4) The high pressure phase at the quenched and unloaded sample from $9.8 GPa$ and $\sim 500^\circ C$, respectively is identified as a hexagonal phase which is closely related to the high pressure of Zr (i.e., ω -Zr).

(5) The zero-pressure volume change for the transition of ZrH_2 -I (tetragonal) \rightarrow ZrH_2 -II (hexagonal) is approximately 11.5%.

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