Compression Studies of Single-Crystal SnO_2 and PbO_2 in a Diamond Cell

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ABSTRACT

Compression behaviors of two single-crystal rutile-structure dioxides, SnO_2 (cassiterite) and PbO_2 (plattnerite), were studied in a Merrill-Bassett type diamond cell at room temperature. The samples were compressed in a mixture of 4:1 methanol-ethenol solution with pressure measurements by the ruby scale. A four-circle diffractometer was used to obtain the diffraction patterns of these crystals at high pressures. Compression results on SnO_2 did not show significant lattice distortion, with a slight increase in *c/a* up to 35 kbar. The compression data are in excellent agreement with Hazen and Finger (1981) and in reasonable agreement with Ming and Manghnani (1982). Fitting these data to the Birch-Murnaghan equation gives a bulk modulus (K_o) of 2.24 ± 0.08 Mbar with $K_o' = 6.3$. On the other hand, the rutile-type PbO_2 was found to transform from a tetragonal to an orthorhombic phase above 5 kbar. The cell parameters *a*, *b* and *c* of this phase have different linear compressibility. This phase is different from the reported orthorhombic phases of lead dioxides (α-PbO_2). It could represent an intermediate distorted phase which occurs during the transformation from the β-PbO_2 to the α-PbO_2 phase. The bulk modulus of PbO_2 was determined to be 1.34 ± 0.06 Mbar by fitting the data to the Birch-Murnaghan equation. A linear relationship was found to exist between the bulk sound velocity and mean atomic weight of the rutile-type dioxides.

1. INTRODUCTION

Our knowledge of the planet Earth is limited by the fact that the Earth's interior is inaccessible. An indirect approach must be adopted in order to understand the chemical compositions and physical conditions of the Earth's interior. For instance, an equation of state (EOS) of a mineral can be determined by high-pressure, high-temperature apparati. The EOS, coupled with seismic observations, can thus provide constraints on the elastic properties of the constituting phases of the Earth's interior.

In order to yield detailed information on the structure and precise measurements on the lattice parameters of a phase, one has to rely on single-crystal compression data. The

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single-crystal type diamond cell was first invented by Merrill and Bassett (1974) to study the compression behavior of some important geological materials. The cell was later modified by Hazen *et al.* (1981) to carry out experiments at pressures exceeding 200 kbar. The developmental history, operating procedure and applications of the single-crystal diamond cell have been fully described by Hazen and Finger (1982). The technique utilizes the four-circle X-ray diffractometer which has yielded valuable data on the structural details of the crystals (Hazen, 1985).

SiO_2 is one of the most abundant coumpounds on Earth. Because the high-pressure polymorphic transitions in SiO_2 might place significant constraints on the evolution of the interior of the Earth and of the other terrestrial planets, its P-T (temperature-pressure) phase diagram and the physical properties of the various polymorphs have been widely investigated (see Liu and Bassett, 1986 for a detailed description). Similarly, the nature of the phase behavior of several analogous dioxides at high pressures has also been extensively studied (Liu, 1982; Ming and Manghnani, 1982). Studies of dioxides at high pressures in general are of great interest to physicists, chemists, and material scientists investigating the phase transformations and elastic properties of these materials.

Dioxides form a variety of crystal structures depending on the size of the cations. Detailed phase relationships of the various dioxides are described in Liu and Bassett (1986) and some of the important dioxides hace been studied by Ming and Manghnani (1982). However, their results are not consistent in terms of identifying the high-pressure phase (such as ZrO_2) and predicting a post-rutile phase transition (such as SiO_2). Their identification of a high-pressure phase is based on the diffraction patterns of polycrystalline samples which may not give reliable structural information. Hence, a four-circle single-crystal goniometer with structural refinement is needed to resolve the discrepancies in phase relations of dioxides mentioned above.

There have been relatively few static compression data on single-crystal dioxides except for some rutile-type (Hazen and Finger, 1981), and some SiO_2 polymorphs (Levien *et al.*, 1980; Levien and Prewitt, 1981). Normally, the cell parameters of single-crystals can be determined very accurately (within ± 0.001 Å) by this method. Thus compression study of single-crystal dioxides is important not only in detecting subtle structural changes of a compound during compression but also crucial in determining the mechansim of a phase transition.

We have carried out a systematic compression study of the dioxides in a single-crystal type diamond cell. In this report, we will describe briefly the technique of the single-crystal compression in a diamond cell using four-circle goniometer X-ray diffraction. This technique will then be used to study the compression behaviors of some dioxides. Through these studies, we are looking for a systematic trend in the compression behaviors of cation polyhedra in various structural types of dioxides. The phase relationships and the mechanism of post-rutile transformation are also briefly discussed.

2. EXPERIMENTAL METHOD

SnO_2 and PbO_2 single-crystals were requested from the Smithsonian Museum, Washington, D. C. Electron microprobe examination indicated that the crystals used in this experiment consisted mostly of Sn and Pb, respectively. Prior to the experiments, the crystals were examined with a four-circle diffractometer to determine their structures and lattice parameters. The crystals were then carefully chopped to small chips with dimensions of $100 \times 100 \times 50\ \mu m$ for the experiment. A Merrill and Bassett type diamond cell (Figure 1) was used to generate pressure. A T301 stainless steel gasket (250 μm thick) was indented by the diamonds and a hole (200 μm) was drilled in the center of the indentation. The crystal was mounted in the gasket hole with ruby chips (15 μm in size) for pressure measurements (Barnett *et al.*, 1973; Huang, 1992). Pressure was measured each time before and after the diffrcation signal was collected. Several ruby chips were measured in order to test the hydrostaticity of the run. A mixture of 4:1 methenol-ethenol solution was used as a pressure medium. After the sample was loaded, the orientation of the sample in the diamond cell was determined preliminarily by a precession camera. The cell was then mounted on the four-circle diffractometer to determine the structure and lattice parameters. A sophisticated and specified program was needed to drive the four-circle diffractometer and to collect and analyze the diffraction signals. It took 1 to 2 days for the data acquisition of each pressure increment. A flow chart shows the experimental procedure is outlined in Figure 2. The experiments were carried out at the Geophysical Laboratory, Carnegie Institute. A detailed description of the principle, the methods and procedure of the experiment was reported by Li (1992).

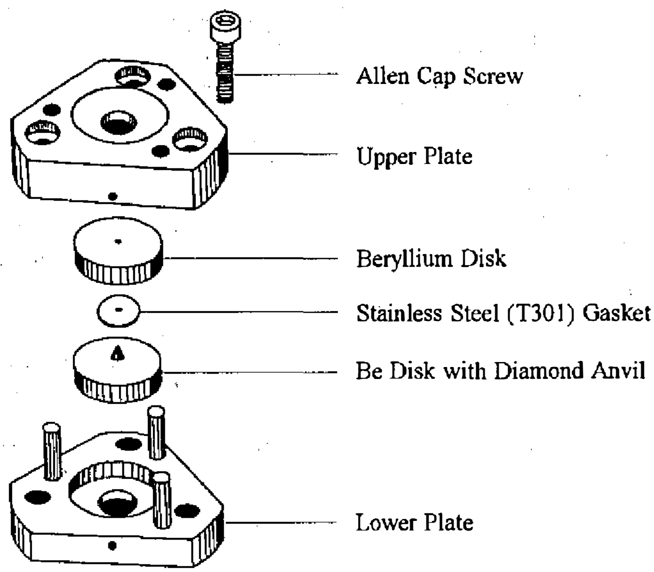

Fig. 1. Single-crystal type diamond anvil cell (from Hazen and Finger, 1982).

Experimental Method

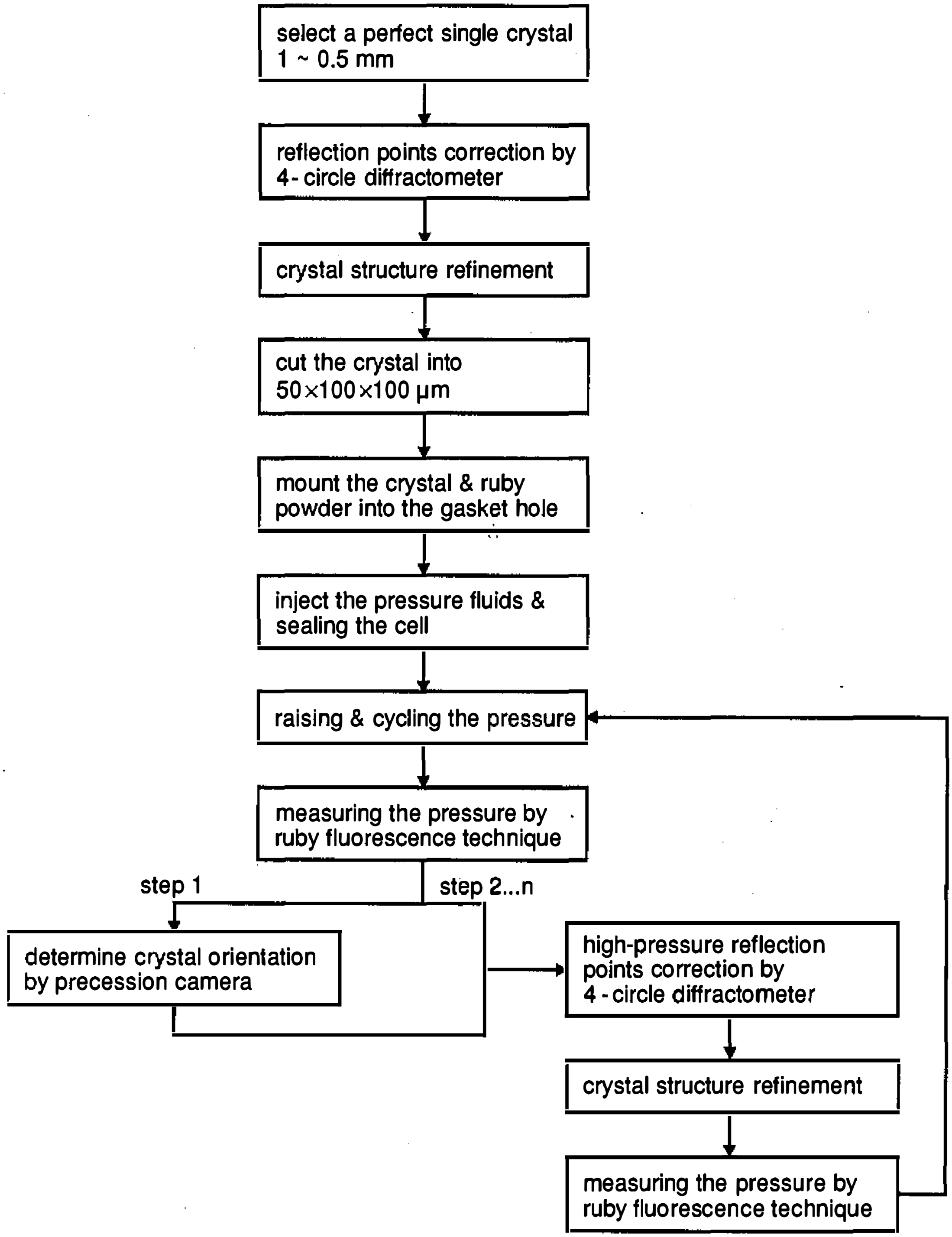

Fig. 2. Flow chart of the procedure for single-crystal four-circle diffractometry diamond cell compression experiments.

3. RESULTS

In single-crystal compression experiments, error in the calculation of lattice parameters is of the order of 0.1%, which results in an uncertainty of 0.3% in molar volume determination. Uncertainty in pressure estimation by the ruby fluorescence is less than 0.5 kbar.

Compression of the single-crystal SnO_2 remains rutile structure up to 30 kbar. The experiment ended with further compression to 36 kbar where the crystal was found to be in contact with both of the diamond anvils. Results of the cell parameters, *a*, *c*, *c/a*, and molar volume, V, of SnO_2 at various pressures are listed in Table 1 and the variations of *a*, *c*, and V/V_0 with pressure are shown in Figure 3.

In PbO_2, the cell parameter a splits into two cell parameters *a* and *b* above 5 kbar. The compression results of PbO_2 up to 21.2 kbar are listed in Table 2. The variations of cell parameters, *a* and *b*, and relative change of cell parameters with pressure are shown in Figure 4. Cell parameters, *a* and *c* , decrease with pressure while the new cell parameter, *b*, increases slightly up to 18 kbar and then decreases with pressure (Figure 4b). The molar volume shows a slightly higher compressibility at about 5 kbar (Figure 6). The change from tetragonal to orthorhombic phase in PbO_2 above 5 kbar has never been reported.

4. DISCUSSIONS

4.1 Compressibility of SnO_2

From Figure 3, it is obvious that the linear compressibility of *a* is higher than that of *c* in SnO_2. This results in an increase of *c/a* ratio with pressure. Results on the variation of *c/a* in SnO_2 with pressure observed in our study are consistent with that obtained by Hazen and Finger (1981). This implies that the lattice of cassiterite, despite being somewhat distorted, still remains its rutile-type structure during the compression. Lattice distortion of this type is best observed by the single-crystal lattice refinement method in the single-crystal experiment which is greatly superior to the powder method.

Our compression data are in excellent agreement with those obtained in single-crystal measurements by Hazen and Finger (1981). These results are combined and fit to the Birch-Murnaghan equation:

$$P = 3/2\, K_0\, [(V_0/V)^{7/3} - (V_0/V)^{5/3}]\{1 - 3/4(4 - K_0')[(V_0/V)^{2/3} - 1]\}$$

where P is the pressure in Mbar, K_0 and K_0' are isothermal bulk modulus (in Mbar) and its derivative, respectively. The bulk modulus thus obtained is 2.24±0.08 Mbar assuming that K_0' is 4. These data are not sufficient to further constrain the value of K_0'. Ming and Manghnani (1982) have reported the compression data of powdered SnO_2 up to 330 kbar. Their data are in reasonable agreement with the Birch-Murnaghan equation of state using

Table 1. Compression Results of Single-Crystal SnO_2

a (Å)	*c* (Å)	V (Å³)	*c/a*	P (kbar)
4.737	3.186	71.496	0.6726	0.001
4.7375	3.186	71.495	0.6725	1.0
4.733	3.1846	71.345	0.6728	6.2
4.728	3.183	71.15	0.6732	12.5
4.721	3.181	70.915	0.6738	18.0
4.716	3.180	70.72	0.6743	22.7
4.713	3.1787	70.60	0.6744	28.2
4.711	3.1780	70.53	0.6746	30.0
4.7103	3.1782	70.515	0.6747	36.4

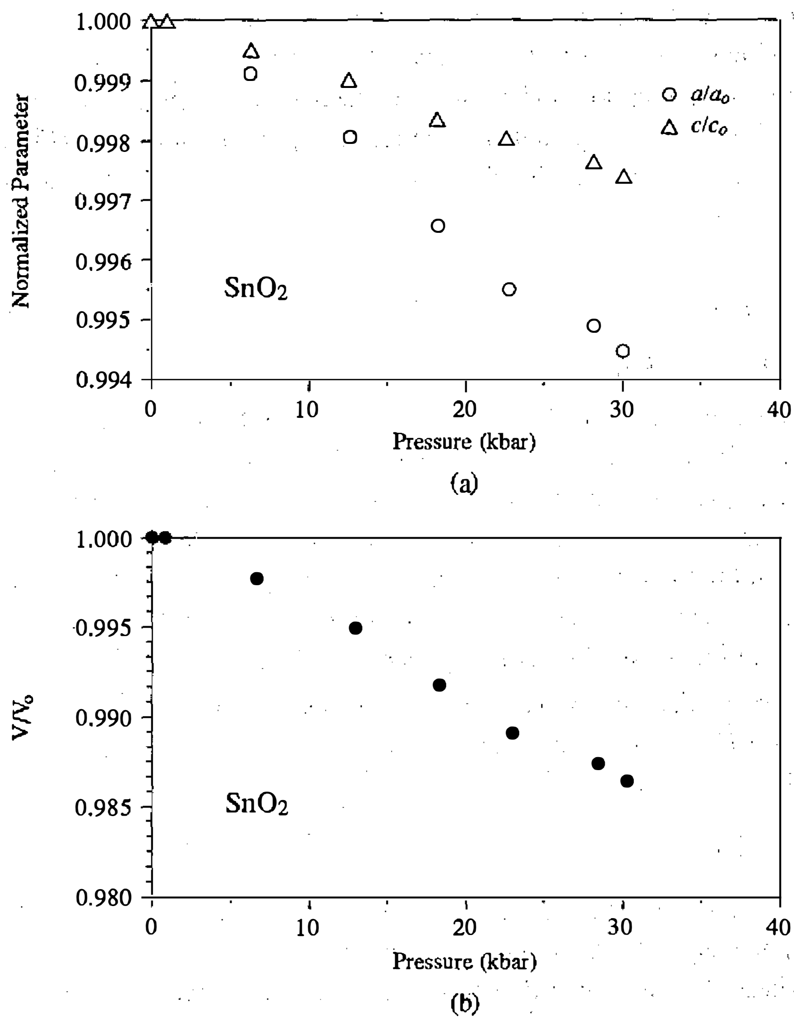

Fig. 3. Variation of normalized (a) cell parameters, a/a_o and c/c_o and (b) molar volume V/V_o of SnO_2 with pressure.

Table 2. Compression Results of Single-Crystal PbO_2

a (Å)	*b* (Å)	*c* (Å³)	V (Å³)	P (kbar)
4.9564	4.9564	3.3872	83.210	0.001
4.9454	4.9444	3.3843	82.753	4.6
4.9413	4.9464	3.3851	82.737	7.7
4.9336	4.9522	3.3836	82.669	10.2
4.9162	4.9544	3.3832	82.404	13.3
4.9014	4.9557	3.3823	82.156	18.4
4.8928	4.9523	3.3812	81.929	21.2

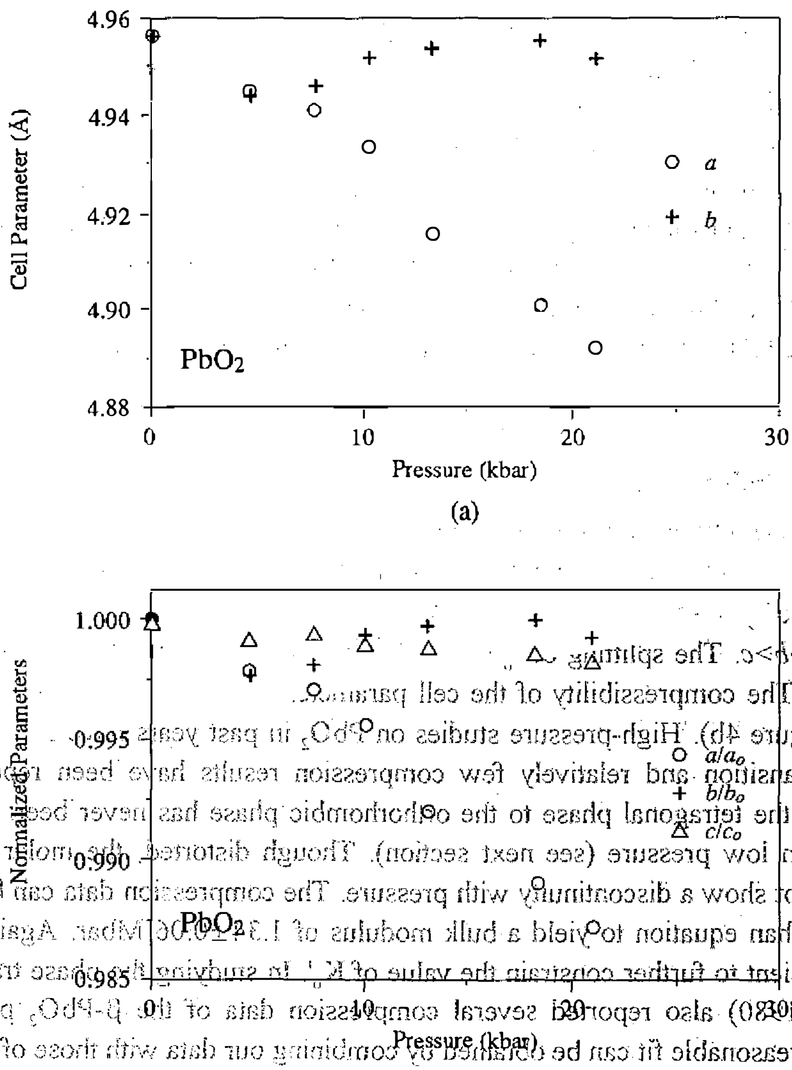

Fig. 4. Variation of (a) cell parameters *a*, *b*, and (b) a/a_o, b/b_o, c/c_o of PbO_2 with pressure.

the above values (K_0=2.24, K_0'=4). However, when the compression data of SnO_2 obtained by the single-crystal method (including this study and Hazen and Finger, 1981) and by the powder method (Ming and Manghnani, 1982) are combined, a K_0 of 2.24 Mbar and K_0'=6.3 fit best for the Birch-Murnaghan equation (Figure 5). The K_0 is 10% higher than that reported by Liebermann (1973) determined by the ultrasonic method. The discrepancy may be due to the porosity and anisotropy of the sample in ultrasonic measurement. Clendenen and Drickamer (1966) have studied the compression behaviors of some rutile-type dioxides powder by the Bridgman anvil. The compression data of SnO_2 reported by them are not suitable for fitting the Birch-Murnaghan equation. They have reported a convex-upward compression curve for SnO_2, which is in contrast with the normal concave-upward compression curve. The discrepancy can be attributed to the nonhydrostatic condition in their experiments. They have used LiF, Ag and Al as pressure calibrants which are much more compressible than SnO_2. This has resulted in the pressure inhomogeneity (Jameison and Olinger, 1971) where soft materials respond to uniaxial compression sooner than hard materials. As a consequence, the sample is less compressed while the pressure calibrants are highly compressed at low pressures. At sufficiently high pressures, the sample and pressure calibrants are compressed more uniformly due to the relaxation of the uniaxial loading (Huang and Bassett, 1984). Hence, at low pressures, the sample behaves very incompressibly while at high pressures it shows normal compressibility (see Figure 6, Ming and Manghnani, 1982). Similar abnormal compression curve of MnO_2 reported by Clendenen and Drickamer (1966) may also be due to this effect.

4.2 Compressibility of PbO_2

In PbO_2, the tetragonal crystal (rutile structure, or the β-PbO_2 phase) is observed to transform into an orthorhombic phase by the splitting of a_o-parameter to a and b above 5 kbar (Figure 4). Refinement on the cell parameters of this phase yields three orthorgonal axes with $a \sim b > c$. The splitting of a_o to a and b becomes more prominent with pressure (Figure 4a). The compressibility of the cell parameters increases in the following order: $b < c << a$ (Figure 4b). High-pressure studies on PbO_2 in past years have concentrated on the phase transition and relatively few compression results have been reported. This distortion of the tetragonal phase to the orthorhombic phase has never been reported to occur at such low pressure (see next section). Though distorted, the molar volume of PbO_2 does not show a discontinuity with pressure. The compression data can be fit to the Birch-Murnghan equation to yield a bulk modulus of 1.34±0.06 Mbar. Again, our data are not sufficient to further constrain the value of K_0'. In studying the phase transitions of PbO_2, Liu (1980) also reported several compression data of the β-PbO_2 phase up to 100 kbar. A reasonable fit can be obtained by combining our data with those of Liu (1980) for K_0=1.34 Mbar and K_0'=0.5. A value of K_0'=0.5 is abnormally low compared with other rutile-type dioxides (cf. K_0'=6.8 for TiO_2 by Manghnani (1969) and K_0'=6.3 for

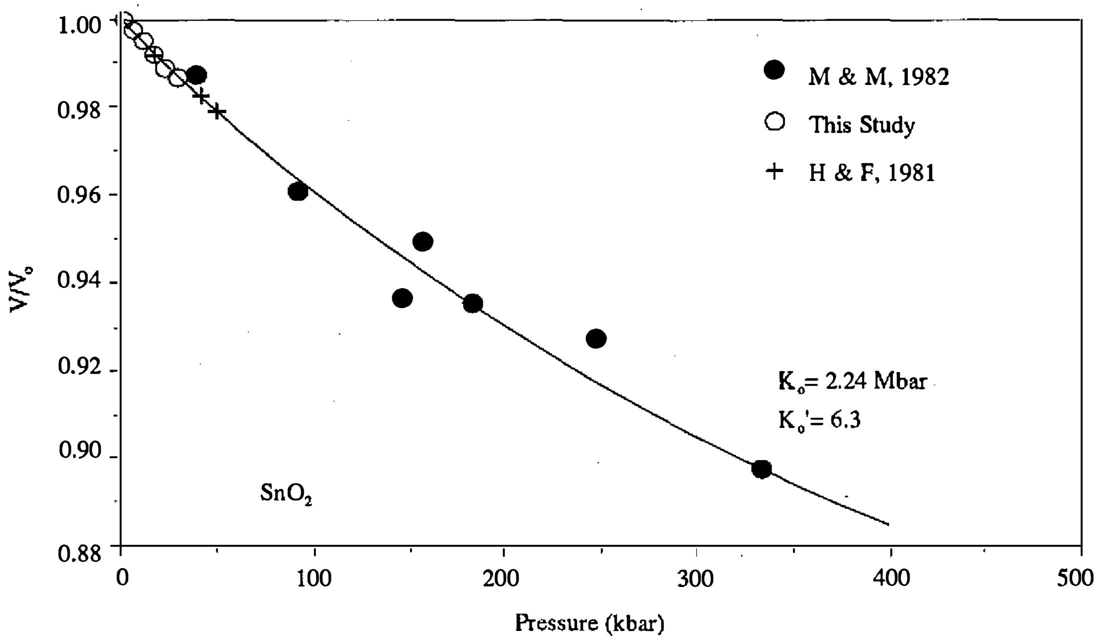

Fig. 5. Compressibility of cassiterite at room temperature. Fitting the compression data including this study (open circle), Hazen and Finger (1981, plus sign), and Ming and Manghnani (1982, solid circle) to Birch-Murnaghan equation yields a curve with K_o= 2.24 Mbar with K_o'= 6.3.

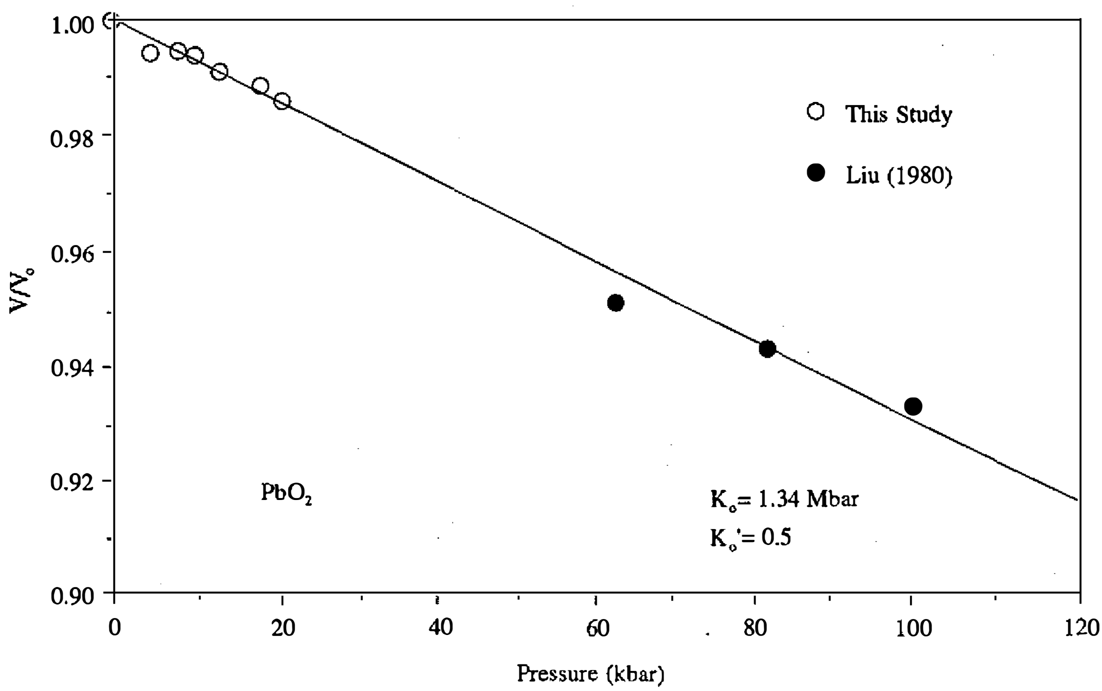

Fig. 6. Compressibility of β-PbO_2 at room temperature. Fitting our data (open circle) and Liu (1980, solid circle) to Birch-Murnaghan equation yields K_o= 1.34 Mbar with K_o'= 0.5.

PbO_2 in this study). It is likely that the effect of the distortion becomes more prominent at high pressure and the compression curve does not reflect the behavor of a normal rutile-type dioxide. The lattice distortion of rutile PbO_2 to the orthorhombic phase is relatively minor to be resolved by the powdered diffraction method. Hence, the β-PbO_2 phase which exists metastably at ~100 kbar observed by Liu (1980) may not be tetragonal. Apparently, more single-crystal compression work is needed to justify this and to provide more reliable data on the equation of state of PbO_2.

4.3 Phase transformation in PbO_2

In PbO_2, the orthorhombic phase which occurs above 5 kbar is different in lattice parameters and molar volume from the previous reported orthorhombic phase (α-PbO_2) (Rueschi and Chana, 1975; Dachille and Roy, 1960; White *et al.*, 1961; Liu, 1980; Yagi and Akimoto, 1980; Ming and Manghnani, 1982). A comparison of cell parameters and molar volume between this phase and the α-PbO_2 phase was described by Li (1992). Phase transition between β-PbO_2 and α-PbO_2 was reported to occur at ca. 10 kbar in the previous studies (Ruetschi and Cahan, 1957; Dachille and Roy, 1960; and White *et al.* 1961). However, detailed experimental methods were not reported and pressure measurements were ambiguous in the studies of Ruetschi and Cahan (1957) and Dachille and Roy (1960). The transition pressure (10 kbar, at room temperature) reported by White et al (1961) was an extrapolated value from their high-temperature and high-pressure results. It is likely that the transition from the β-PbO_2 to the α-PbO_2 phase at room temperature may be affected by the kinetic effect. The α-PbO_2 phase (i.e. reported by White *et al.*, 1961) was not found in this experiment up to 22 kbar. In a separate run, the phase transition to a-PbO_2 was optically observed to take place at about 47 kbar.

Though structure varys at 5 kbar, the volume changes nearly continuously with the pressure in PbO_2 (Figure 6), indicating a possible second order phase transformation. It is likely that the lattice was distorted during the compression which results in the splitting of the *a*-parameter. On the basis of the hard-sphere model, phase transition in ionic crystals is governed by Pauling's rule, i.e. the relative size of the cations and anions. Prewitt (1982) has argued that the contribution of cations to the structural change is much more significant than the anions in ionic bonding compounds. Ida (1976), on the other hand, proposed that anions are more compressible than cations and the phase transition may thus depend on the compressibility of the anions. However, detailed calculations based on the hard-sphere model indicate that neither of the models can account for the very small amount of change in the *c*-parameter (~10^{-3} Å) of PbO_2. Hazen and Finger (1981) proposed that violating the polyhedral bulk modulus-volume relationship (Hazen and Finger, 1979) and inverse relationship in the rutile-type dioxides may be due to the fact that these compounds have higher covalency. Hence, the hard-sphere model may not be applicable in this case. Other factors such as the nonspherical electron configurations of ions, metal-metal interactions may also play an important role in the lattice distortion (Baur and

Khan, 1971). The distortion of the tetragonal to orthorhombic phase observed in this study may also involve an intimately twinned array of domains, similar to that reported by Hara and Nicol (1979). Detailed description of the mechanism of the phase transition in PbO_2 will be reported elsewhere (Li *et al.*, in prep).

4.4 Limitation of the Single-Crystal Compression

Single-crystal compression studies in a diamond cell suffer from two serious limitations. Firstly, in a routine experiment, the pressure is limited to less than 70 kbar (Hazen and Finger, 1982) despite the fact that pressure as high as multimegabar can be generated in the diamond cell (Xu *et al.*, 1986). This is due to that the single-crystal has to be large enough to give significant diffraction signals and the difficulty in maintaining the hydrostaticity in the diamond cell above 100 kbar (Piermarini *et al.*, 1973). This limitation can be partly overcome by using synchrotron radiation as the X-ray source. In addition, using inert-gas solids as pressure transmitting media could provide a hydrostatic environment in a diamond cell (Finger *et al.*, 1981). Recently, synchrotron radiation has been applied to study the EOS and phase transition of single-crystal He up to 233 kbar (Mao *et al.*, 1990). Although technical difficulties in loading the sample cryogenically (Mao and Bell, 1980) are often encountered, this technique has opened up a feasible way for producing an accurate EOS of minerals to a wider P and T regime. Another problem in single-crystal compression is that in-situ structural refinement of the highly absorbing materials is always difficult. For instance, the structural refinement of PbO_2 is very difficult because of the absorption of X-rays by Pb. This has sometimes hindered the interpretation of the phase transition. Therefore, improvement in the structural refinement of the single-crystal diffraction and its coulping with synchrotron radiation may be needed to provide us with reliable compression data, to detect phase transitions, and to resolve the mechanism of the transformation.

5. IMPLICATIONS

In past years, numerous efforts have been made to find systematics in the compression behavior of materials, as in the case of Birch's law which relates the bulk sound velocity with the density of minerals (Birch, 1961), and bulk modulus-volume relation for polyhedra (Hazen and Finger, 1979). Some of the empirical formulae such as the seismic equation of state (Anderson, 1967) have also been proposed for application to the elastic behaviors of minerals in the Earth's interior. A typical example is the plot of the bulk sound velocity (Φ) versus mean atomic weight ($\overline{M}$) of minerals by Liebermann (1973) who discovered the following relationship:

$$\Phi\,\overline{M}^n = \text{constant}$$

in some of the rutile-type dioxides (SiO_2, GeO_2, TiO_2 and SnO_2) with n=1/2, in accord-

Table 3. List of mean atomic weight ($\overline{M}$), molar volume (V), bulk modulus (K_o) and density (ρ) of various rutile-type dioxides for the determination of bulk sound velocity (Φ)

Dioxides	$\overline{M}$ (g)	V (Å^3)	K_o (Mbar)	ρ (g/cm^3)	Φ (km/s)
SiO_2	20.03	46.40	3.06[a]	4.300	8.436
TiO_2	26.63	62.408	2.19 ±0.03[b]	4.251	7.177
MnO_2	28.98	55.156	2.75[c]	5.234	7.251[c]
GeO_2	34.86	55.330	2.62 ±0.04[b]	6.277	6.461
NbO_2	41.64	70.311	2.34[d]	5.899	6.298
RuO_2	44.36	62.640	2.70 ±0.06[b]	7.054	6.187
SnO_2	50.30	71.496	2.24 ±0.08[e]	7.008	5.654
PbO_2	79.73	83.210	1.34 ±0.06[e]	9.546	3.747

a. Weidner *et al.*, 1982
b. Hazen and Finger, 1981
c. This study, calculated from empirical formula: Φ (km/s) = 9.34 – 0.0721 $\overline{M}$ (g)
d. Sumino and Anderson, 1984
e. This study, single-crystal compression results

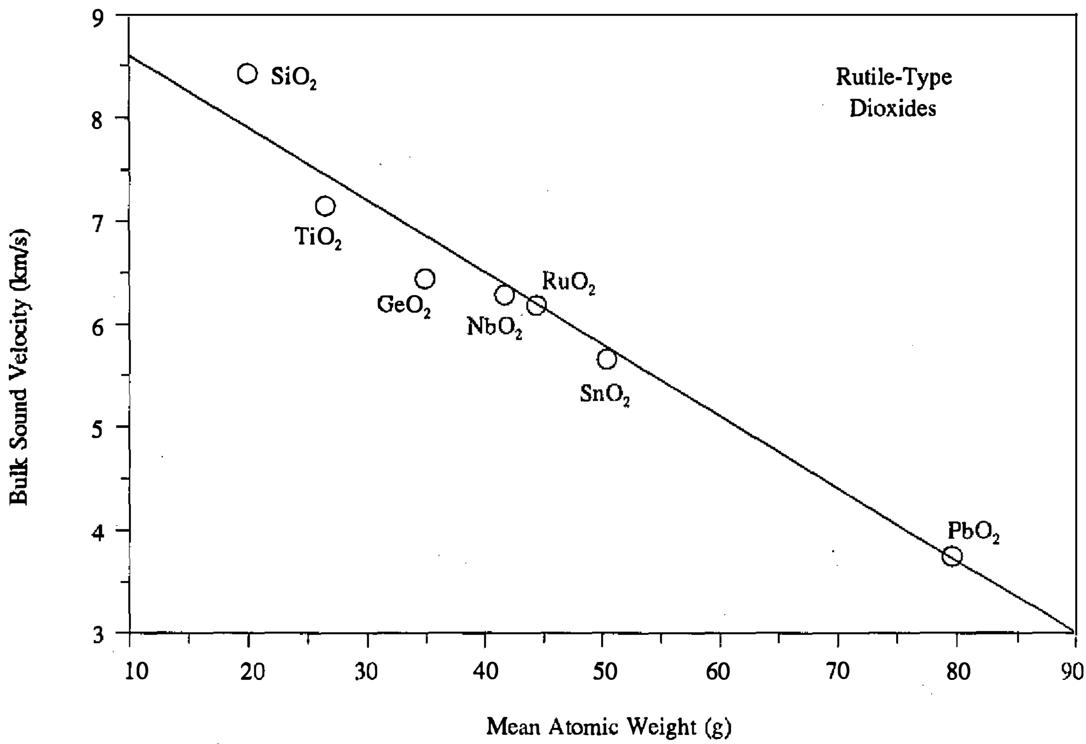

Fig. 7. Plot of bulk sound velocity (Φ) versus mean atomic weight (M) for rutile-type dioxides. A linear relationship: Φ (km/s) = 9.34 – 0.0721 $\overline{M}$ (g) is found to exist for these oxides.

ance with the observation of Shankland (1972). Using the available data (Table 3), we have found a similar relationship exists for the rutile-type dioxides. However, a linear relationship fits better in the bulk sound velocity versus mean-atomic-weight plot as seen in Figure 7. In some of the calculations, we have used isothermal bulk modulus in place of the adiabatic bulk modulus K_s for the determination of bulk sound velocity (Table 3). At room temperature, the difference between the two is less than 1% which is within the error of the determination of the bulk modulus itself. The significance of this relation is still unknown.

Anderson (1972) has proposed that KV_0 = constant holds for alkali halides and fluorides. A $K \sim V^{-1}$ law seems to hold for some rutile-type dioxides such as GeO_2 and SnO_2 (Liebermann, 1973). Our data do not support that KV_0 = constant but favor a linear relationship between molar volume and bulk modulus in rutile-type dioxides. The correlation is not as good as that between bulk sound velocity and mean atomic weight. The linear relation shown in Figure 7 is:

$$\Phi \text{ (km/s)} = 9.34 - 0.0721\ \overline{M} \text{ (g)}$$

The theoretical basis for this relationship is not clear. This empirical formula is then used to infer the less well-known bulk modulus of MnO_2 to be 2.75 Mbar since the bulk modulus cannot be obtained from the compression data of Clendenen and Drickamer (1966) due to the effect of pressure inhomogeneity (see 4.1). Further research on the compression study of MnO_2 is required to justify the validity of the formula proposed above.

6. SUMMARY

Reliable data obtained from single-crystal compression can reveal subtle change in the cell parameter of the lattice. This report describes results on the compression behaviors of two rutile-type dioxides, SnO_2 and PbO_2. A slight lattice distortion which is manifested by the increase in the *c/a* ratio with pressure is observed in SnO_2 up to 30 kbar. It remainsrutile structure with a K_0 of 2.24 Mbar. On the other hand, a phase transition from the rutile to an orthorhombic structure is observed at 5 kbar for PbO_2. The cell parameters of the orthorhombic phase demonstrate different compressibility with a being the most compressible axis while *b* and *c* are only slightly compressed up to 22 kbar. The molar volume changes continuously during the phase transition. Fitting the compression data to the Birch-Murnghan equation gives a bulk modulus of 1.34 Mbar. The orthorhombic phase found in this study has different molar volume and lattice parameters from the α-PbO_2. This phase may be treated as the distortion of the rutile structure of PbO_2 during compression. A linear relationship is found to exist between the bulk sound velocity and mean atomic weight among the rutile-type dioxides as: Φ (km/s) = 9.34 – 0.0721 $\overline{M}$ (g).

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單晶 SnO_2 及 PbO_2 之鑽石砧壓研究

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摘　要

本實驗藉鑽石高壓砧對兩金紅石結構之單晶雙氧化物，錫石 (SnO_2, cassiterite) 及塊黑鉛礦 (PbO_2, plattnerite) 進行常溫之壓縮研究，樣本置於靜水壓狀態，其所受之壓力經由紅寶石螢光測壓法量出。利用四環單晶繞射儀以收集繞射資料。錫石在被加壓到 35 仟粑 (kbar) 之過程中，其結構仍保持不變，只有晶格常數 c/a 之比值隨壓力增高而變大，其彈性模量 (bulk modulus) 定爲 2.24 ± 0.08 百萬粑 (Mbar)。塊黑鉛礦則在 5 仟粑時由正方晶系轉變爲斜方晶系。轉變後之斜方相之三軸呈現不同之壓縮係數。由於在相轉變時摩耳體積之改變並無不連續之現象推測該斜方相爲由金紅石 (β-PbO_2) 轉變爲 α-PbO_2 之過渡相。塊黑鉛礦之彈性模量可定爲 1.34 ± 0.06 百萬粑，綜合上述結果與其它資料，發現在金紅石結構之單晶雙氧化物內，其整體聲速 (bulk sound velocity) 和平均原子量 (mean atomic weight) 間有線性關係存在。