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Compression Study of Goethite at Room Temperature

상온에서 괴타이트에 대한 압축 연구

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ABSTRACT : A natural FeOOH-goethite was compressed up to 9.5 GPa at room temperature using a DIA-type large volume apparatus with synchrotron radiation. Energy dispersive x-ray diffraction method was employed to measure its compressibility and NaCl was used for high pressure determinations. Bulk modulus was determined to be 131.1 (±5.8) GPa by the Birch-Murnaghan equation of state with K_0' fixed to 4. The present result is not in accord with the previous measurements, which vary from 111 to 147.9 GPa.

Key words : goethite, large volume apparatus, synchrotron radiation, bulk modulus

요약 : 천연시료 FeOOH-괴타이트에 대한 압축성을 측정하기 위하여 방사광과 라지 발륨 기기를 이용하여 상온에서 압축실험을 시행하였다. 에너지분산 x-선 회절법을 적용하였고 압력은 NaCl을 이용하여 측정하였다. 버치-머내한 상태방정식을 이용하여 계산된 체적탄성률은 131.1(5.8) GPa이었고 이때 K_0'은 고정된 값 4를 이용하였다. 현재 측정된 값은 이전에 발표된 값(111~147.9 GPa)과 일치하지 않고 차이를 보이고 있다.

주요어 : 괴타이트, 라지 발륨 기기, 방사광, 체적탄성률

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Introduction

Goethite is naturally abundant phase, existing as a hydrous alteration product as a weathering artifact of various rocks. This phase is a prototypical hydroxide which crystallizes in the orthorhombic system with space group Pbnm. Goethite structure is characterized by a slightly distorted hexagonally close packed oxygen framework with iron occupying two-thirds of the octahedral sites. In this respect, goethite is isostructural with diaspore (AlOOH) by replacement Fe with Al.

Goethite has been used extensively in the preparation of Fe_2O_3-maghemite crystals in magnetic storage media technology because of its topological relations to the Fe_2O_3-hematite structure (Williams and Guenther, 1996). In addition to this, hydrous minerals at the Earth interior have been considered as the host materials of hydrosphere geophysically (Ringwood and Major, 1967; Liu, 1987). Therefore, the equation of state (EOS) of various hydrous minerals including goethite has been studied by many investigators theoretically as well as experimentally in many conditions (e.g., Meade and Jeanloz, 1990; Duffy *et al.*, 1991; Tyburczy *et al.*, 1991; Fei and Mao, 1993; Xu *et al.*, 1994; Mao *et al.*, 1994). A natural goethite-FeOOH, one of the hydrous minerals, was compressed for its equation of state (EOS) refinement up to 9.5 GPa at room temperature conditions using a DIA-type large volume apparatus. Compression data thus obtained has been reported in this paper.

Experiments

Compression was performed using a DIA-type (i.e., DIA-6), the large-volume compression apparatus designed for *in-situ* x-ray diffraction (XRD) studies. In the use of the DIA-6 press, energy-dispersive x-ray diffraction (EDXRD) technique was adopted using white radiation from the superconducting wiggler magnet at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. In this press, the force of a uniaxial ram is transmitted to six anvils which advance into the solid pressure medium that is cubic in shape.

White radiation from the wiggler enters to the gap between anvils and the diffracted x-ray exits via to the opposite side gap. The incident x-ray beam was collimated to 100 × 200 μm in size, and the diffracted beams were collected at a fixed angle set-up of the solid state intrinsic Ge-detector (i.e., 2θ = 7.378(9)). The counting time for XRD spectrum collection was 5 min. in live-mode. Pressure was determined using the well known equation of state (EOS) for NaCl (Decker, 1971). Five XRD peaks of NaCl, (111), (200), (220), (222), and (420) were used for pressure calculations. The uncertainty of the pressure values ranges from 0.1 to 0.3 GPa, which are attributed mainly to the peak searching processes, within the acceptable statistical variations. An alcohol mixture of methanol-ethanol (ME) in the volume ratio of 4:1 was used as the pressure medium for the sample chamber hydrostacity. Other details on DIA-6 press were given elsewhere (Wang *et al.*, 1998; Chen *et al.*, 1998; Utsumi *et al.*, 1998; Zhang, 2000). A natural polycrystalline FeOOH-goethite sample used for the present compression experiment was the same as used previously in the diamond anvil cell (DAC) study (Kim and Yi, 1997).

Results and Discussions

At 0.1 MPa (i.e., 0.0001 GPa), the peaks of (110), (120), (130), (111), (140), (130), (041), (211), (221), (150), (160), (002), and (061) were used to calculate the lattice parameters of goethite: a = 4.613, b = 9.973, and c = 3.017 Å (Table 1). This is compared with that of previously reported one by Kim and Yi (1997) on the same sample (i.e., a = 4.665, b = 9.938,

Table 1. XRD data of FeOOH-goethite with pressures

P, GPa	a, Å	b, Å	c, Å	V, Å^3	V, cm^3/mole	V/V$_0$
0.0001	4.613	9.973	3.017	138.80	2.0.90	1.000
0.90	4.596	9.957	3.014	137.93	20.77	0.994
1.84	4.578	9.937	3.008	136.84	20.60	0.986
2.64	4.568	9.921	3.003	136.09	20.49	0.981
3.47	4.549	9.899	2.995	134.87	20.30	0.972
4.29	4.531	9.885	2.993	134.05	20.18	0.966
4.88	4.519	9.871	2.988	133.29	20.07	0.960
5.68	4.507	9.853	2.980	132.33	19.92	0.953
6.28	4.500	9.876	2.971	132.04	19.88	0.951
7.18	4.489	9.830	2.976	131.32	19.77	0.946
7.92	4.463	9.758	2.961	128.95	19.41	0.929
8.84	4.471	9.751	2.949	128.57	19.36	0.926
9.54	4.447	9.767	2.950	128.13	19.29	0.923
9.44*	4.450	9.779	2.950	128.37	19.33	0.925
8.81*	4.458	9.812	2.956	129.30	19.47	0.932
8.19*	4.476	9.814	2.963	130.16	19.60	0.938
7.69*	4.483	9.819	2.968	130.65	19.67	0.941
6.84*	4.490	9.846	2.976	131.56	19.81	0.948
6.02*	4.506	9.864	2.985	132.67	19.97	0.956
4.81*	4.530	9.891	2.989	133.93	20.16	0.965
3.06*	4.535	9.891	2.994	134.30	20.22	0.968
0.0001*	4.613	9.970	3.018	138.80	20.90	1.000

*unloading process

c = 3.005 Å). This discrepancy would be attributed to the different instrumental accuracy; In DAC experiment, goethite was mixed with MgO as the pressure precursor. Therefore, some of the Bragg peaks from two phases overlapped and this evoked some obstacles in profile fitting. Furthermore, another possible reason is the stress induced differently during the sample grinding process (Haines *et al.*, 2001). In order to remove such residual stress in the powder sample, annealing at some high temperatures either in air or in inert gas is needed. However, goethite sample preparation in both experiments did not follow this procedure. The other possibility would be the different powder averaging due to the different sample amount used in both experiments.

One cycle of the run (i.e., loading and subsequent unloading processes) has been performed up to 9.54 GPa and a series of the selected spectra in the loading process is shown in Fig 1. For each spectrum, the peak positions were determined by the Gaussian peak fitting of the diffracted intensity. All diffraction peaks shift with pressure maintaining their peak shape all the way, so lattice parameters at high pressures can be refined with accuracy and confidence. When the alcoholic mixture of ME as the pressure medium is used, this fluid transforms to solid at 11 GPa and results in the non-hydrostacity of the sample chamber (Piermarini *et al.*, 1973). This could affect the XRD peak broadening, but the pressure range of present experiment is within this limit.

With increasing pressure, the variations of lattice parameter are shown in Table 1. The present results differ from the previous one (see Table 2, Kim and Yi, 1997). In the previous experiment, only five peaks of (110), (120), (130), (040), and (111) were observed from the

Table 2. Bulk moduli of diaspore and goethite

Compounds	K, GPa	K_0'	Reference
AlOOH (diaspore)	170.3	5.2	Ruoff and Vanderborgh (1993)
	230	4.0	Xu *et al.*, (1994)
	167.5	4.0	Mao *et al.*, (1994)
	134	4.0	Grevel *et al.*, (2000)
	148		Winkler *et al.*, (2001)
FeOOH (goethite)	147.9	4.0	Kim and Yi (1997)
	111	4.0	Nagai *et al.*, (2003)
	131.1	4.0	This study

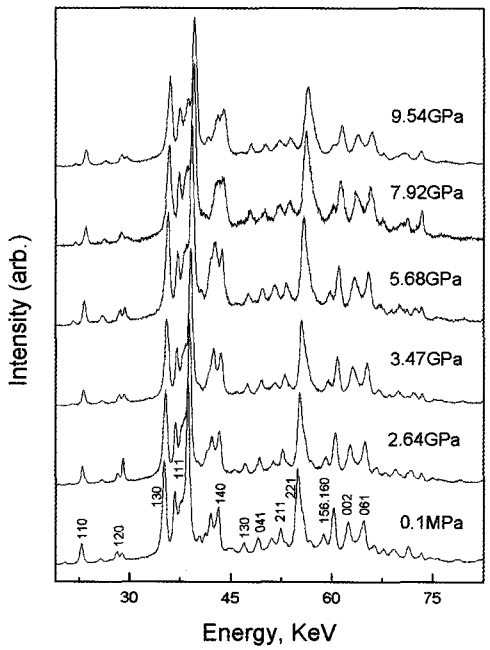

Fig 1. A series of spectra of goethite with pressures recorded in high pressure run.

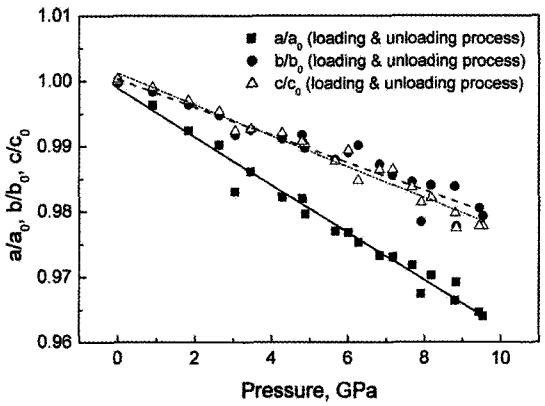

Fig 2. Axial compression of goethite with pressure.

high pressure runs above 8.1 GPa. This was attributed to the solidification of the pressure medium and subsequent spread of the diffracted x-ray intensity. Reduced XRD peaks' intensity might also be caused from the thinning of the sample at high pressures. Among these XRD peaks, only (111) peak is related to the lattice parameter c (i.e., c/c_0). Therefore, this parameter of c-axis could not be determined with sufficient accuracy (i.e., c/c_0 column in Table 2, Kim and Yi, 1997). According to the present results (Table 1 and Fig 2), the compressional tendency is anisotropic, where the a-axis is more compressible than the b- and/or c-axes. The a-axis compression prevails over so that the volume compression is determined by compression along this direction. This behavior would be caused by the fact that there exists the vacant space along a-axis in this structure.

Normalized volume compression trend with pressure is shown in Fig 3. Based on Table 1 and Fig 3, bulk modulus (i.e., K_T) was determined by the Birch-Murnaghan EOS (i.e., $P=1.5K_0(X^{-7} - X^{-5})[1 - 0.75(4 - K_0')(X^{-2} - 1)]$), where $X= [V(T,P)/V(T,0)]^{1/3}$ when K_0' is assumed to be 4. The present result is compared with previously reported one and those of its structural analog, diaspore-AlOOH (Table 2). In the compression study of diaspore, Xu *et al.*,

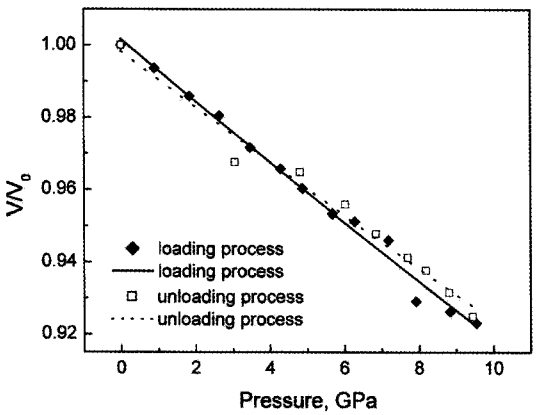

Fig 3. Compressibility of the unit cell volume of goethite with pressure.

(1994) explained that almost all compression occurs by shortening of Al-O bonds as in the case of corundum (i.e., Al_2O_3) on the basis of the similar bulk modulus of diaspore (i.e., K_0=230 GPa) and corundum (i.e., 226 GPa, Sato and Akimoto, 1979). However, this value of 230 GPa is much higher than any other reported ones in Table 2, even though their compression work was done in the non-hydrostatic conditions. Therefore, the extended application to the structural analogue of hematite (Fe_2O_3) related to goethite should be digressed (Kim and Yi, 1997) because speculation basis of Xu *et al.*, (1994) is merely their similarities of bulk moduli. At the same time, similar argument was applied to ilmenite ($FeTiO_3$) which is closely related to the hematite structure, but this should not be valid any more either.

Crystallography of goethite can be expressed as follows: $FeO_3(OH)^{3-}$octahedra are linked by their pinnacles to form the chain. Fe^{3+} is in the octahedral coordination between O and $(OH)^{-1}$ which are arranged in hexagonal closed packing (i.e., hcp) in the plane of b- and c-axis. Therefore, compression takes place along the bond between Fe and O as well as within OH, which results in the anisotropy against the applied pressure. As pointed out by Nagai *et al.*, (2003), the hydrogen bond is significantly directed parallel to the a-axis so that the bulk compression is involved by shortening the hydrogen bonds oriented nearly along the a-axis. This speculation confirms the anisotropic compression of the lattice parameters observed in the high pressure experiments on goethite structured minerals in Table 2.

Present result (i.e., 131.1 GPa) obtained up to 9.5 GPa explains appropriately the reason of previous high value (i.e., 147.9 GPa) from DAC experiment performed on the same natural sample (see Table 1, Kim and Yi, 1997). However, present one is higher than 111 GPa of Nagai *et al.*, (2003) by 20 GPa, which was performed in the DAC using the image plate on the pure synthetic sample. As pointed out by Nagai *et al.* (2003) in their compression up to 24 GPa, a sudden strain broadening of diffracted peaks occurs above 11 GPa when a 4:1 methanol : ethanol pressure medium solidifies (Piermarini *et al.*, 1973; Mao *et al.*, 1994). This might be attributed to their bulk modulus determination, however, it is hardly to mention the exact discrepancy sources such as sample volume differences, preferred orientations in the sample assembly, pressure determination method differences, sample chemistry and so on.

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