Anomalous behavior and phase transformation of α-GaOOH nanocrystals under static compression*

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The structural compression mechanism and compressibility of gallium oxyhydroxide, α-GaOOH, are investigated by *in situ* synchrotron radiation x-ray diffraction at pressures up to 31.0 GPa by using the diamond anvil cell technique. The α-GaOOH sustains its orthorhombic structure when the pressure is lower than 23.8 GPa. The compression is anisotropic under hydrostatic conditions, with the *a*-axis being most compressible. The compression proceeds mainly by shrinkage of the void channels formed by the coordination $GaO_3(OH)_3$ octahedra of the crystal structure. Anomaly is found in the compression behavior to occur at 14.6 GPa, which is concomitant with the equatorial distortion of the $GaO_3(OH)_3$ octahedra. A kink occurs at 14.6 GPa in the plot of finite strain f versus normalized stress F, indicating the change in the bulk compression behavior. The fittings of a second order Birch–Murnaghan equation of state to the P–V data in different pressure ranges result in the bulk moduli $B_0 = 199(1)$ GPa for $P < 14.6$ GPa and $B_0 = 167(2)$ GPa for $P > 14.6$ GPa. As the pressure is increased to about 25.8 GPa, a first-order phase transformation takes place, which is evidenced by the abrupt decrease in the unit cell volume and *b* and *c* lattice parameters.

Keywords: gallium oxyhydroxide, high pressure, synchrotron radiation, equation of state

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1. Introduction

The pressure responses of hydrogenous materials represent an interesting research topic in various fields of science. The high-pressure behavior of H_2O is of fundamental importance in both condensed matter and planetary physics. The multiform ways in which H_2O molecules may link through hydrogen bonding bring about a series of phases in ice and fluid water under varying pressures and temperatures.[1,2] In both small organic molecules and supramolecular assemblies, the pressure responses of hydrogen bonding are important not only for predicting the possible crystal structure under pressure, but also, more generally, for solving the problems relating to polymorphism, crystal engineering, structure-properties correlations, and reactivity of these molecular solids in many aspects.[3,4] Another class of important hydrogen-bearing material is hydroxides and oxyhydroxides of metals. These materials become a research target because they show complicated structural and property changes relating to hydrogen bond interactions. Diverse behaviors, such as pressure-induced amorphizations, phase transitions, partial (H-sublattice) amorphizations, etc., have been reported under high pressures.[5–7]

Among these materials is diaspore, α-AlOOH, which presents an ideal model system for high-pressure studies, as it combines relatively highly symmetric (orthorhombic) and a relatively small unit cell with simple chemistry and a nonlinear hydrogen bond of intermediate strength.[8,9] However, there have been found large discrepancies in the high-pressure investigations on diaspore. Mao *et al.* reported a bulk modulus $B_0 = 167.5$ GPa (obtained from energy-dispersive powder x-ray diffraction experiments) up to 25.5 GPa with a 4:1 methanol:ethanol mixture serving as a pressure-transmitting medium.[10] Xu *et al.* gave a bulk modulus $B_0 = 230$ GPa via similar techniques but without a pressure-transmitting medium.[11] Grevel *et al.* reported the (P, V, T)-equation of state of diaspore from data collected up to 7 GPa and 1073 K and found $B_0 = 134$ GPa.[12] However, recent *in situ* single-crystal synchrotron x-ray diffraction at high pressures with complementary theoretical analyses indicates that a bulk modulus $B_0 = 150$ GPa sounds more reasonable.[8,9] In addition to the interest in the fields of material physics and crystallography, diaspore is also of great relevance to geophysics and geochemistry because it is one of the simplest model structures of hydrous minerals, thereby providing some insights into processes of water transport in subduction zones at depths ranging from the Earth's surface to the deep mantle.[13]

As a direct analogue of diaspore, α-GaOOH bears much

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resemblance to its low-period counterpart. They both belong to the group 13 oxyhydroxide family (MOOH, M = Al, Ga, and In), and α-GaOOH is isostructural to diaspore.[14] High-pressure studies of α-GaOOH can provide insights into the intrinsic natures of the group 13 oxyhydroxides under pressures, such as the phase stabilities, the phase evolutions, the H bonding characteristics, etc., through observing the structures and physical properties with continuous changes of the distance between the two neighboring oxygen atoms ($r_{O\cdots O}$), which affects the strengths of hydrogen bonds within these materials. Moreover, as a wide band gap metal oxyhydroxide, α-GaOOH itself has aroused considerable interest, owing to its special properties with good application prospect in many fields, such as light-emitting, gas sensing, catalytic, electrochemistry, etc. For instance, in GaN-based blue light-emitting diode, strong light extraction improvement can be achieved with top and sidewall α-GaOOH nanorod arrays.[15] The α-GaOOH nanorods exhibited superior photocatalytic activity and stability as compared with commercial TiO_2 (P25, Degussa Co.) in both benzene and toluene degradation.[16] In this context, the high pressure studies of α-GaOOH may also help to reveal and expand its potential application scope under extreme conditions. Although the high-pressure metastable polymorph (with a distorted rutile-type structure) of GaOOH, β-GaOOH, has been reported to be compressed to a maximum pressure of up to 35 GPa under quasi-hydrostatic conditions,[17,18] to the best of our knowledge, similar high pressure studies of α-GaOOH seem to be lacking in the literature.

In the present study, the structural compression behaviors and compressibility of diaspore-type α-GaOOH are investigated by *in situ* synchrotron radiation x-ray diffraction at pressures up to 31.0 GPa by using the diamond anvil cell (DAC) technique. The primary goal of this study is to provide a better understanding of the nature of the hydrogen bonding and the structural compression mechanism of the group 13 oxyhydroxides under high pressures.

2. Experimental section

Fine powders of α-GaOOH nanocrystals used in this study were prepared by the solvothermal synthesis method. The details of the synthesis were described elsewhere.[19] The crystal structures of the samples were confirmed by the powder x-ray diffraction pattern obtained on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (λ = 1.5406 Å) in ambient conditions.

High-pressure experiments were carried out by using a Mao–Bell type diamond anvil cell (DAC) with 0.50-mm diamond culets. A T301 stainless steel gasket was pre-indented to a thickness of about 0.10 mm by the diamonds and then drilled to produce a 0.15-mm diameter cavity, which acted as the sample chamber. The fine powders of α-GaOOH were placed in the gasket hole together with several small ruby chips to determine the pressure by using the standard ruby fluorescent technique.[20] A 16:3:1 mixture of methanol-ethanol-water was used as the pressure-transmitting medium. By monitoring the separation and widths of both R1 and R2 fluorescent lines, the quasi-hydrostatic conditions over the whole pressure range were confirmed.

In situ angle-dispersive x-ray diffraction (ADXRD) measurements were performed at 4W2 High-Pressure Station of Beijing Synchrotron Radiation Facility (BSRF). Monochromatic radiation at a wavelength of 0.6199 Å was adopted for pattern collection. Diffraction patterns were recorded with a mar345 image plate detector and were integrated and corrected for distortions by using the FIT2D software.[21–23] The XRD patterns were then indexed and refined by using the EXPGUI software.[24,25] All experiments were carried out at room temperature.

3. Results and discussion

The orthorhombic lattice of α-GaOOH belongs to space group *Pbnm*, with the formula units $Z = 4$ and the cell parameters $a = 4.5325(5)$ Å, $b = 9.7922(8)$ Å, $c = 2.9737(2)$ Å in ambient conditions. It can be built from the so-called 'double rutile strings' of edge-sharing $GaO_3(OH)_3$ octahedra, as illustrated schematically in Fig. 1. These double strings are arranged parallel to the c-axis and are connected via common oxygen corners. The OH groups form hydrogen bonds in the (001) crystalline planes across the channels formed by the coordination octahedra, with the O–O vectors tilted by about 26.8° with respect to the a-axis, and the H atoms displaced by about 12.5° with respect to the O–O direction.[26] The O–H bond length is about 0.995 Å. All the oxygen atoms are arranged in a slightly distorted hexagonal close packing, with the gallium atoms occupying some of the octahedral sites.

The evolutions of the representative x-ray diffraction patterns under high pressures up to 31.0 GPa are shown in Fig. 2. It is evident that all the diffraction peaks shift to higher angles with the increase of pressure, indicating a decrease in unit cell volume. As pressure increases, the peaks become broader, less intense, and some merged together. The x-ray diffraction data at each pressure are indexed and refined to obtain valid lattice parameters and cell volumes. In Figs. 2(b) and 2(c) are shown the refinements of the XRD data obtained at ambient pressure (Cu Kα radiation) and at 17.1 GPa (synchrotron radiation), respectively, as examples. The results are summarized in Table 1. Over the whole pressure range, no new diffraction peak emerges.

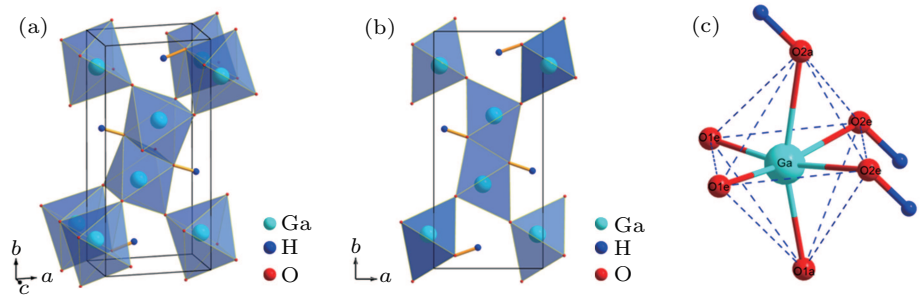


Fig. 1. (color online) Schematic illustrations of the crystal structure of diaspore-type α-GaOOH for (a) an arbitrary view and (b) a projection view along the c axis, and (c) distorted $GaO_3(OH)_3$ octahedron. There are two independent oxygen sites: O2 in ambient conditions covalently bonded to hydrogen (O–H bond), and O1 characterized by a weak H···O bond; in the selected octahedron one can distinguish between O1a and O2a atoms at the axial positions and two O1e and two O2e atoms at the equatorial positions.

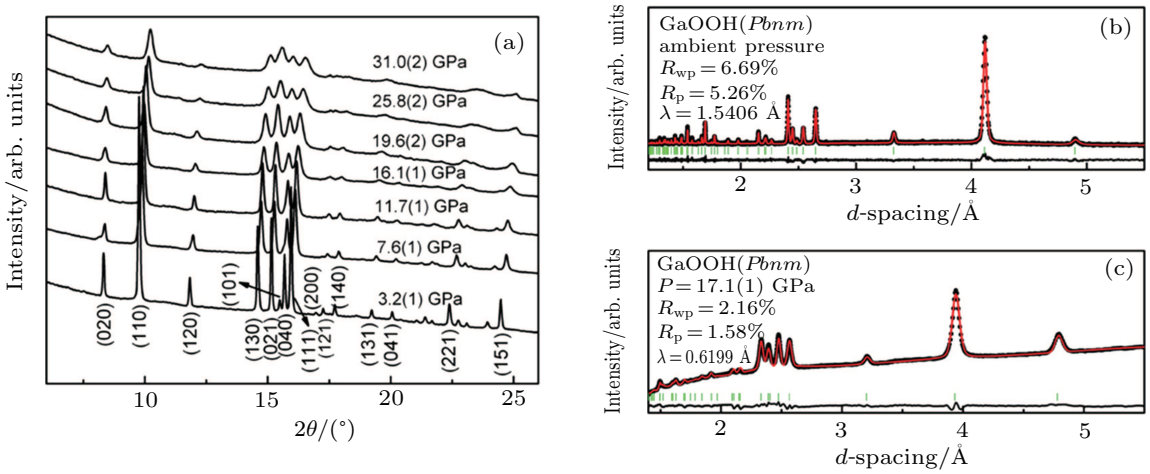


Fig. 2. (color online) Representative x-ray diffraction patterns of α-GaOOH at (a) some high pressures (up to 31.0 GPa) and are indexed and refined by using EXPGUI software, (b) ambient pressure, and (c) 17.1 GPa.

Table 1. Unit-cell parameters and atomic positions obtained from refinements of the XRD data acquired at ambient pressure and 17.1 GPa with weighted R factors.

P/GPa	Lattice parameters/Å	Atomic positions				R factors	
		Atom	x	y	z	R_p	R_{wp}
0.0001	$a = 4.5325(5)$ Å $b = 9.7922(8)$ Å $c = 2.9737(2)$ Å $V = 131.98(6)$ Å^3	Ga O1 O2	0.0477(8) 0.7319(8) 0.1668(7)	–0.1431(5) 0.1902(5) 0.0577(3)	0.25 0.25 0.25	5.26%	6.69%
17.1(1)	$a = 4.3134(6)$ Å $b = 9.5541(8)$ Å $c = 2.8913(5)$ Å $V = 119.15(7)$ Å^3	Ga O1 O2	0.0667(1) 0.699(8) 0.284(4)	–0.1372(4) 0.2970(3) 0.1014(2)	0.25 0.25 0.25	1.58%	2.16%

In Fig. 3(a), the normalized unit-cell parameters show the anisotropies of the linear compressibilities. The a axis is apparently much more compressible than the b and c axes, while the compressibilities of the b and c axes are nearly equal in the low-pressure range: the compressibility of c axis is slightly higher than that of b axis. On the one hand, hydrogen bonds are formed in the a–b plane, thus, the c axis is less affected by the change in strength of hydrogen bond. On the other hand, the direction of hydrogen bond is closer to the direction of the a axis. From Fig. 1(b), it can also be seen that the compression of the a axis mainly involves the relative bending of the double strings against the common corners. The compression of b axis involves the deformation and distortion of the double strings as can be also expected for the compression of c axis. Since large open channels exist among the coordination octahedra, it is reasonable that a higher compression occurs in the a axis, rather than in the other two axes. In conclusion, the compression of the crystal structure proceeds mainly by contracting the channels, involving the shortening of the hydrogen bonds, rather than the slimming down of the $GaO_3(OH)_3$ octahedra. It is also noteworthy that a sudden decrease may be observed in the b and c unit-cell parameters at about 25.8 GPa,

indicating a change in the crystal structure.

Figures 3(b) and 3(c) display the compression curves shown as the plot of finite strain f against normalized stress F (F–f plot) and as the plot of unit cell volume against pressure (P–V plot), respectively. The F–f plot is useful to visualize slight anomalies of equation of state, which are difficult to find in the P–V plot. For Birch–Murnaghan equation of state, f and F are defined as follows:

$$f = [(V_0/V)^{2/3} - 1]/2, \quad (1)$$

$$F = P/[3f(1+2f)^{5/2}]. \quad (2)$$

From Fig. 3(b), it can be seen that the F–f plot shows a positive slope at low pressures. A kink occurs at 14.6 GPa, after which the F–f plot shows almost horizontal variation until the pressure reaches 23.8 GPa. Such a kink in the F–f plot indicates the change in the bulk compression behavior.[17] When the pressure is further increased to above 25.8 GPa, an abrupt change appears in both the F–f plot and the P–V plot (Fig. 3(c)). This abrupt shrinkage of the unit cell volume may stem from the sudden decrease in the b and c parameters as shown in Fig. 3(a). The isothermal bulk modulus is calculated using the P–V data. The experimental data are fit to the second-order Birch–Murnaghan equations of state (BM-EOS) in the pressure ranges: below 14.6 GPa, between 16.1 GPa and 23.8 GPa, and above 25.8 GPa, respectively (see Fig. 3(c)). For the data obtained below 14.6 GPa, the bulk modulus B_0 obtained from fitting is 199(1) GPa. The unit cell volume V_0 obtained from fitting is 128.47(4) Å^3. From conventional crystal chemical arguments, it may be empirically assumed that the value of V_0B_0 is approximately constant within isostructural compound.[27] Hence, the compressibility increases with increasing unit cell volume. In this study, the unit cell volume of α-GaOOH is larger than that of diaspore (117.96 Å^3) and smaller than that of goethite (140.45 Å^3).[9,28] Thus the value of the bulk modulus may be expected to be between those of diaspore (150 GPa) and goethite (111 GPa). However, an unexpected higher bulk modulus has been obtained for α-GaOOH in this study. The product V_0B_0 of α-GaOOH is about 44% higher than that of diaspore. For the data obtained between 16.1 GPa and 23.8 GPa, the bulk modulus B_0 obtained from fitting is 161(2) GPa, considerably smaller than that obtained from the data below 14.6 GPa. The corresponding unit cell volume V_0 obtained from fitting is 130.34(1) Å^3. For the data obtained above 25.8 GPa, the bulk modulus B_0 obtained from fitting is 245(1) GPa. The unit cell volume V_0 obtained from fitting is 124.78(2) Å^3. In a word, α-GaOOH retains its lattice structure to about 23.8 GPa, with a change in compressibility occurring at about 14.6 GPa. With further increasing the pressure, α-GaOOH undergoes a first-order phase transformation at about 25.8 GPa, which is indicated by the discontinuous changes in the unit cell volume and b and c parameters. However, the overall structure of the XRD patterns obtained above 25.8 GPa is almost the same as those obtained at lower pressures. Thus the phase transformation may be tentatively addressed as an isostructural one as observed in α-FeOOH.[29] Nevertheless, owing to the complexities in the possible configurations of the hydrogen atoms and hydrogen bonds at high pressures, the high-pressure phase may still have an orthorhombic structure, but probably with a different space group. Further neutron diffraction experiments on single crystalline samples of α-GaOOH seem inevitable to determine the exact space group of the high pressure phase.

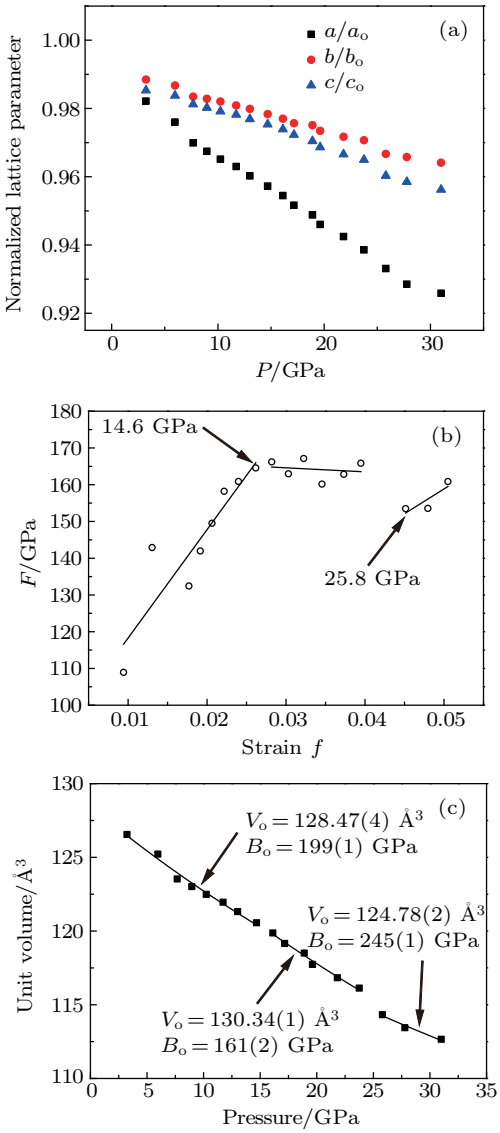


Fig. 3. (color online) (a) Pressure-dependent normalized unit-cell parameters up to 31.0 GPa. (b) Plot of the normalized pressure F against the Eulerian strain f, with a kink at 14.6 GPa and a sudden change at 25.8 GPa. The solid lines show the linear fittings of the data. (c) Pressure-dependent unit-cell volume, fitted by using second order Birch–Murnaghan equations of state. The data below 14.6 GPa, between 16.1 GPa and 23.8 GPa, and above 25.8 GPa, are fitted separately.

Our observation results can be compared with the earlier

experimental results of the high-(P, T)-stability of α-GaOOH. A high-pressure phase, β-GaOOH, which is metastable under normal conditions, could be obtained at P = 8.5 GPa and T = 400 °C in presence of supercritical aqueous vapor,[30] or at P = 19 GPa and T = 1400 °C by laser heating.[17] Thus it can be assumed that the transition from α- to β-GaOOH is kinetically hindered at ambient temperature. In other words, temperature plays an important role in the phase transformation. However, considering the large open channels within the lattice (Fig. 1), it is noteworthy that α-GaOOH can remain stable at pressures more than 6.8 GPa–17.3 GPa above the transition pressure without showing any collapse of the lattice.

Similar changes of the elastic properties have been previous reported for distorted rutile-type oxyhydroxides, such as δ-AlOOH, δ-AlOOD,[31] β-GaOOH, InOOH, and β-CrOOD.[17] With increasing pressure, the a and b axes of δ-AlOOH stiffen at 10 GPa. Identical behavior is found in δ-AlOOD but the change in compressibility is observed at a slightly higher pressure of 12 GPa. The changes are observed at 15 GPa in β-GaOOH and InOOH and at 4 GPa in β-CrOOD. In these distorted rutile-type oxyhydroxides, the change in compressibility is attributed to the symmetrization of the hydrogen bonds. However, no evidence for the symmetrization of the hydrogen bonds in α-GaOOH is found in this study. Instead, significant distortion of $GaO_3(OH)_3$ octahedron is observed, similar to that found in α-FeOOH,[29] which is isostructural to α-GaOOH and also shows the change in compressibility at a similar pressure ($\sim$ 16 GPa) as discussed below.

Although it is hardly possible to determine the exact hydrogen position unambiguously by XRD techniques experimentally, the information about the strength of the hydrogen bond can be inferred from the interatomic O–O distance. Systematical investigations on the relationships between O–O and O–H distances within the system containing hydrogen bonds have been carried out by the careful examination of the low temperature neutron diffraction data.[32] It has been shown that the interatomic distances of the hydroxyl O–H and the hydrogen bond O$\cdots$H species can be derived through the bond valence concept by using the experimentally measured atomic positions of the involved oxygen atoms.[33]

The interatomic distances obtained from refinement of the XRD data, as well as those of the O–H and O$\cdots$H bonds derived through valence bond concept, are shown in Fig. 4. It can be seen that up to 14.6 GPa the Ga–O distances remain almost invariable except Ga–O2e distance, which decreases slightly from 1.89 Å to 1.80 Å. This confirms the low compressibility of the GaO_6 octahedron. As the pressure is further increased, abrupt changes in the interatomic distances occur. The Ga–O2e distance decreases abruptly at 14.6 GPa, and gradually increases thereafter. In contrast, the Ga–O1e distance increases drastically to 2.68 Å in a narrow pressure range from 14.6 GPa to 18.9 GPa, and decreases slightly with increasing pressure. Similar trends may be found in the H–O distances. At pressures up to 14.6 GPa the bond length of the hydroxyl O2–H decreases and that of the hydrogen bond O1$\cdots$H increases slightly. When the pressure is further increased, an anomaly occurs in each of the two cases. After that, when pressure is increased to higher than 18.9 GPa, the distance of O2–H increases and that of O1–H decreases with pressure slightly. It can be seen that severe deformation of the GaO_6 octahedron takes place in the equatorial position, with the O atoms covalently bonded with H moving close to the central Ga atoms and the O atoms in H$\cdots$O bonds moving oppositely. These phenomena strongly indicate that the profound changes take place at 14.6 GPa, with the crystal structure being retained. Presumably the changes may be related to the geometrical configuration of the hydrogen bond system as expected for other hydrogenous system such as portlandite ($Ca(OH)_2$).[34] From this viewpoint, it may be inferred that the elastic properties of the compressed sample vary concomitantly with the structural change of the GaO_6 octahedron. However, the high uncertainty of the hydrogen position, together with the strongly bent hydrogen-bond angle, precludes us from drawing any concrete conclusions on the pressure-dependent behaviour of the hydrogen bond.

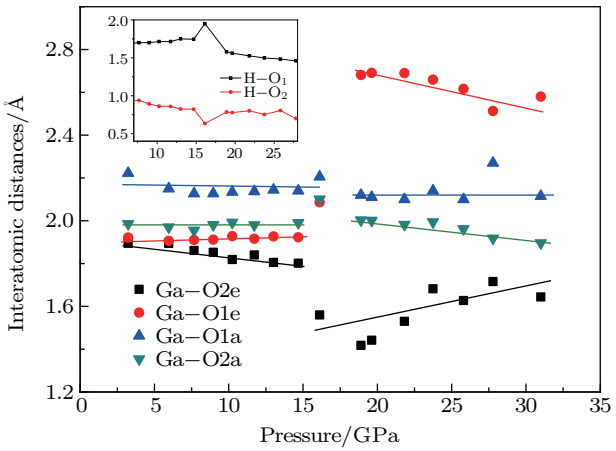


Fig. 4. (color online) Pressure-dependent interatomic distances. The individual O2–H and O1$\cdots$H bond lengths calculated based on experimentally determined atomic positions of gallium and oxygen atoms and the valence bond rule are shown in the inset. The solid lines serve only as guides to the eyes.

In many isostructural oxides (e.g., olivines, spinels, and perovskites), the high-pressure behavior changes systematically depending on the cation size. In hydroxides and oxydroxides, however, the behaviors are much more complicated and show greater variety, presumably due to the hydrogen bond network in the structure. This complexity is enhanced due to the existence of both proton-ordered and -disordered forms as well as metastable crystalline and amorphous phases. Isostructural to α-GaOOH, diaspore (α-AlOOH) and goethite (α-FeOOH) have attracted considerable research interest.

Like the results in this study, the structure of diaspore remains stable at pressures up to at least 51.5 GPa at ambient temperature, which is 30 GPa higher than the transition pressure to δ-AlOOH found in quenched high-pressure high-temperature experiments.[8] The compression of α-AlOOH is also anisotropic and largest for the *a* axis. In both α-AlOOH and α-GaOOH, the structural response to pressure is mainly due to the shortening of the hydrogen bond, with the hydrogen bonds becoming more symmetric with increasing pressure, but a complete symmetrization is far from being reached in the investigated pressure range. On the contrary, hydrogen bond symmetrization may occur in α-FeOOH, concurrent with a first-order electronic transition resulting from the Fe^{3+} high-to-low spin crossover at above 45 GPa.[29] Moreover, the elastic properties of α-FeOOH also encounter a change at a similar pressure (16 GPa) to that found in α-GaOOH in this work, suggesting that two different equations of state should be applied for the 0 GPa–16 GPa and the 16 GPa–44 GPa pressure ranges. In addition, in the case of α-FeOOH, the difference in compressibility between Fe–O1 and Fe–O2 bonds, which affects the shape of the octahedral $FeO_3(OH)_3$ moiety, is also discovered. The similar high pressure behaviors of α-FeOOH and α-GaOOH may be due to their similar ionic radii. The electrons filling in the 3d orbitals may also play a role, which contributes further, in addition to the cation sizes, to the difference between α-AlOOH and α-GaOOH. Yet, many experimental efforts are required for these oxyhydroxides, in order to obtain reliable data with high precision, which could make it possible to follow pressure-induced changes of the hydrogen bonds and to interrelate them with the lattice distortions.

4. Conclusions

In this work, we perform the high-pressure studies of α-GaOOH nanocrystals by using *in situ* synchrotron x-ray diffraction technique. The orthorhombic lattice of α-GaOOH remains stable up to at least 23.8 GPa. The main structural compression is obtained by the shrinkage of the hydrogen-containing channels. This is accompanied by the compression of the hydrogen bond, which bridges the channels within the (001) lattice plane, being mainly oriented along the *a* axis. The observed abrupt changes in the interatomic distances indicate strongly that severe distortion of the $GaO_3(OH)_3$ octahedron occurs at about 14.6 GPa, which may be related to the rearrangement of the geometrical configuration of the hydrogen bond system. A close examination of the plot of finite strain f versus normalized stress F, indicates that a best fitting of the dependence of the unit cell volume on pressure could be obtained by assuming two separate equations of state for the $P < 14.6$ GPa and $P > 14.6$ GPa pressure ranges. When the pressure is further increased to a pressure higher than about 25.8 GPa, a first-order isostructural phase transformation occurs, which is indicated by the sudden decreasing of the lattice parameters. These studies will be important for further developing a deep insight into hydrogen bond behaviors of group 13 oxyhydroxide systems under high-pressure conditions.

References

[1] Hemley R J, Jephcoat A P, Mao H K, Zha C S, Finger L W and Cox D E 1987 *Nature* **330** 737
[2] Chou I M, Blank J G, Goncharov A F, Mao H K and Hemley R J 1998 *Science* **281** 809
[3] Boldyreva E V 2004 *J. Mol. Struct.* **700** 151
[4] Wang K, Duan D F, Wang R, Liu D, Tang L Y, Cui T, Liu B B, Cui Q L, Liu J, Zou B and Zou G T 2009 *J. Phys. Chem. B* **113** 14719
[5] Meade C and Jeanloz R 1990 *Geophys. Res. Lett.* **17** 1157
[6] Iizuka R, Kagi H, Komatsu K, Ushijima D, Nakano S, Sano-Furukawa A, Nagai T and Yagi T 2011 *Phys. Chem. Miner.* **38** 777
[7] Nguyen J H, Kruger M B and Jeanloz R 1997 *Phys. Rev. Lett.* **78** 1936
[8] Friedrich A, Haussühl E, Boehler R, Morgenroth W, Juarez-Arellano E A and Winkler B 2007 *Am. Mineral.* **92** 1640
[9] Friedrich A, Wilson D J, Haussühl E, Winkler B, Morgenroth W, Refson K and Milman V 2007 *Phys. Chem. Miner.* **34** 145
[10] Mao H K, Shu J, Hu J and Hemley R J 2010 *J. Superhard Mater.* **32** 192
[11] Xu J A, Hu J, Ming L C, Huang E, and Xie H 1994 *Geophys. Res. Lett.* **21** 161
[12] Grevel K D, Burchard M, Fasshauer D W and Peun T 2000 *J. Geophys. Res.: Solid Earth* **105** 27877
[13] Meade C and Jeanloz R 1991 *Science* **252** 68
[14] Sato T and Nakamura T 1982 *J. Chem. Technol. Biot.* **32** 469
[15] Lee H K and Yu J S 2012 *Jpn. J. Appl. Phys.* **51** 102102
[16] Sun M, Li D, Zhang W, Fu X, Shao Y, Li W, Xiao G and He Y 2010 *Nanotechnology* **21** 355601
[17] Sano-Furukawa A, Yagi T, Okada T, Gotou H and Kikegawa T 2012 *Phys. Chem. Miner.* **39** 375
[18] Bolotina, N, Molchanov, V, Dyuzheva, T, Lityagina, L and Bendeliani, N 2008 *Crystallogr. Rep.* **53** 960
[19] Shi L, Zhang J, Wu S, Li Y, Jiang L and Cui Q 2014 *J. Am. Ceram. Soc.* **97** 2607
[20] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91(B5)** 4673
[21] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 *High Press. Res.* **14** 235
[22] Hammersley A P 1997 *ESRF Internal Report* ESRF97HA02T
[23] Hammersley A P 1998 *ESRF Internal Report* ESRF98HA01T
[24] Toby B H 2001 *J. Appl. Cryst.* **34** 210
[25] Larson A C and Von Dreele R B 1994 *Los Alamos National Laboratory Report LAUR* 86-748
[26] Pye M F, Birtill J J and Dickens P G 1977 *Acta Crystallogr. B* **33** 3224
[27] Anderson D L and Anderson O L 1970 *J. Geophys. Res.* **75** 3494
[28] Nagai T, Kagi H and Yamanaka T 2003 *Am. Mineral.* **88** 1423
[29] Xu W, Greenberg E, Rozenberg G K, Pasternak M P, Bykova E, Boffa-Ballaran T, Dubrovinsky L, Prakapenka V, Hanfland M, Vekilova O Y, Simak S I and Abrikosov I A 2013 *Phys. Rev. Lett.* **111** 175501
[30] Nikolaev N A, Lityagina L M, Dyuzheva T I, Kulikova L F, Bendeliani N A and Vereshchagin L F 2008 *J. Alloys Compd.* **459** 95
[31] Sano-Furukawa A, Kagi H, Nagai T, Nakano S, Fukura S, Ushijima D, Iizuka R, Ohtani E and Yagi T 2009 *Am. Mineral.* **94** 1255
[32] Steiner T and Saenger W 1994 *Acta Crystallogr., Sect. B: Struct. Sci.* **50** 348
[33] Steiner T 2002 *Angew. Chem. Int. Ed.* **41** 48
[34] Iizuka R, Yagi T, Komatsu K, Gotou H, Tsuchiya T, Kusaba K and Kagi H 2013 *Am. Mineral.* **98** 1421