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High-pressure behavior of $\beta$-Ga$_2$O$_3$ nanocrystals


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Freestanding nanocrystalline $\beta$-Ga$_2$O$_3$ particles with an average grain size of 14 nm prepared by chemical method was investigated by angle-dispersive synchrotron x-ray diffraction in diamond-anvil cell up to 64.9 GPa at ambient temperature. The evolution of x-ray diffraction patterns indicated that nanocrystalline monoclinic $\beta$-Ga$_2$O$_3$ underwent a phase transition to rhombohedral $\alpha$-Ga$_2$O$_3$. It was found that $\beta$- to $\alpha$-Ga$_2$O$_3$ transition began at about 13.6–16.4 GPa, and extended up to 39.2 GPa. At the highest pressure used, only $\alpha$-Ga$_2$O$_3$ was present, which remained after pressure release. A Birch–Murnaghan fit to the $P-V$ data yielded a zero-pressure bulk modulus at fixed $B_0=228(9)$ GPa and $B_0=333(19)$ GPa for $\beta$-Ga$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ phases, respectively. We compared our results withbulk $\beta$-Ga$_2$O$_3$, and concluded that the phase-transition pressure and bulk modulus of nanocrystalline $\beta$-Ga$_2$O$_3$ are higher than those of bulk counterpart.

I. INTRODUCTION

Monoclinic gallium oxide ($\beta$-Ga$_2$O$_3$), a wide-band-gap semiconductor ($E_g=4.9$ eV), exhibits unique conduction and luminescence properties and thus attracts much research interest due to numerous technological applications.\(^1\)–\(^5\) Recently, considerable effort has been devoted to the study of nanostructured $\beta$-Ga$_2$O$_3$ because of the potential for applications in nanodevices.\(^6\)–\(^10\) In ambient conditions, monoclinic $\beta$-Ga$_2$O$_3$ is the thermodynamically stable form and there are other four metastable structures: $\alpha$-, $\gamma$-, $\delta$-, and $\varepsilon$-Ga$_2$O$_3$.\(^11\) Different forms have different physical properties. For example, the band gap of the $\alpha$-Ga$_2$O$_3$ polymorph is 2.41 eV, much narrower than that of $\beta$-Ga$_2$O$_3$.\(^12\) $\beta$-Ga$_2$O$_3$ can only be found in the work of Lipinska-Kalita et al.\(^16\) They reported the $\beta$- to $\alpha$-Ga$_2$O$_3$ transition, beginning at 6 GPa, in nanocrystalline $\beta$-Ga$_2$O$_3$ embedded in an amorphous silica matrix. However, they also mentioned that the silica glass matrix undergoes structural and density changes within this pressure range,\(^22\),\(^23\) so that it is not yet known if the structural changes are intrinsic to nanocrystalline $\beta$-Ga$_2$O$_3$, or are promoted by anomalous densification among the silica matrix. These results encourage us to re-examine the high-pressure behavior of freestanding $\beta$-Ga$_2$O$_3$ nanoparticles by angle-dispersive x-ray diffraction (XRD) technique.

II. EXPERIMENTS

Monoclinic $\beta$-Ga$_2$O$_3$ nanoparticles were synthesized as follows: 0.7 g GaCl$_3$, 0.8 g NaOH and 4 ml PEG (Mw 400) were first dissolved in 10 ml ethanol, stirred with a magnetic stirrer. The precursory solution was stirred at 60 $^\circ$C for 1 h to yield a transparent solution in an alumina crucible. The solution in the alumina crucible was then heated in a furnace at 900 $^\circ$C for 3 h. The powder was white after annealing treatment. Finally, the white powder was washed using alcohol and centrifuged for three times, and then dried at 70 $^\circ$C. The average crystallite size of Ga$_2$O$_3$ nanoparticles was determined by XRD with a Cu $K\alpha$ radiation and by transmission electron microscopy (TEM).

In situ angle-dispersive XRD measurements of nanocrystalline $\beta$-Ga$_2$O$_3$ were performed at beam line BL-13A in High Energy Accelerator Research Organization (KEK).

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Monochromatic x-ray ($\lambda = 0.42713$ Å) was collimated to $50 \times 50$ μm$^2$ and irradiated at the center of the sample. Diffraction patterns were collected by image plate detector. The samples were compressed into a 120 μm diameter hole drilled in a T301 stainless steel gasket of a Mao-Bell diamond-anvil cell. A mixture of methanol, ethanol, and water in the volume ratio of 16:3:1 was used as the pressure-transmitting medium. The pressures were determined by the ruby fluorescence method.24

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of as-prepared Ga$_2$O$_3$ nanoparticles which was used to identify the structure and to estimate the mean grain size. A Rietveld full profile refinement$^{25}$ confirmed that all the peaks in the XRD pattern corresponded to the monoclinic β-Ga$_2$O$_3$ (space group C2/m). No peaks of any other phases were detected. The refined β-Ga$_2$O$_3$ lattice parameters and cell volume were $a = 12.233(3)$ Å, $b = 3.038(5)$ Å, $c = 5.806(4)$ Å, $\beta = 103.836(4)^\circ$, and $V = 209.514(4)$ Å$^3$, in agreement with the values of bulk sample [$a = 12.233(10)$ Å, $b = 3.038(3)$ Å, $c = 5.807(5)$ Å, $\beta = 103.821(7)^\circ$, and $V = 209.56(4)$ Å$^3$].$^{16}$ The average grain size of nanocrystalline β-Ga$_2$O$_3$ was estimated to be about 14 nm using the Scherrer formula, consistent with the average value of the grain size discerned in the TEM micrograph of Fig. 2(a). Each nanocrystal was roughly spherical and almost composed of a single-crystalline domain, as shown in Fig. 2.

Synchrotron XRD patterns of 14 nm β-Ga$_2$O$_3$ nanocrystal in the compression up to 64.9 GPa and the following decompression down to ambient pressure at room temperature were collected to analyze the pressure-induced phase transitions and to retrieve the isothermal bulk modulus. Some selected XRD patterns, which are characteristic of the whole evolution, are shown in Fig. 3. Diffraction line broadening at high pressure might be originated from nonhydrostaticity caused by solidification of pressure-transmitting medium at pressures above about 16 GPa. The diffraction patterns collected at low pressures correspond well to the monoclinic β-Ga$_2$O$_3$ phase. With increasing pressure, all diffraction peaks systematically shifted toward higher 2θ angles, and some peaks disappeared while new lines emerged. At 16.4 GPa, a new peak [arrowed in Fig. 3(a)] appeared, indicating occurrence of a phase transition. The phase transition proceeded slowly, and above 39.2 GPa, only peaks from the high-pressure phase remained to the highest pressure used in this study. The high-pressure diffraction patterns could be indexed within the $R\bar{3}c$ space group expected for the rhombohedral α-Ga$_2$O$_3$, in accordance with former results.$^{15,16,21}$

At the beginning of phase transition, the (104) and (110) peaks, two strong reflections of α-Ga$_2$O$_3$, were overlapped with the (111) and (111) peaks of the still dominating β-Ga$_2$O$_3$, so the onset pressure of phase transition is imprecisely estimated only according to the appearance of the (113) peak. In order to confirm the pressure range of the β- to α-Ga$_2$O$_3$ phase transition and to determine the lattice parameters, Rietveld refinements were performed on all diffraction patterns recorded during compression and subsequent decompression. The evolution of weight percent for β-Ga$_2$O$_3$ and α-Ga$_2$O$_3$ with pressure is presented in Fig. 4. It is clearly shown that the weight percent of β-Ga$_2$O$_3$ keeps close to 100% below 13.6 GPa. For the pattern at 16.4 GPa, the Rietveld refinement confirmed that β- and α-Ga$_2$O$_3$ phases coexisted with a ratio of 89.7:10.3 in wt %. It is obvious that the phase transition begins in the range of 13.6–16.4 GPa. The β-Ga$_2$O$_3$ was the dominating phase up to 19.8 GPa, and tiny β-Ga$_2$O$_3$ could still be detected at 36.8 GPa, indicating a sluggish transition in a wide pressure range of 13.6–39.2 GPa similar to the range of 6.5–40 GPa for bulk Ga$_2$O$_3$.16

All patterns collected from the decompression sequence only attribute to α-Ga$_2$O$_3$, and the gradual shift of diffraction
pressure during compression. [50x548]lowing lattice parameters of [50x434]GPa and ambient pressure. The refinements yielded the fol-

et al. [50x386]results of Lipinska-Kalita [50x506]ation of the [50x506]/H9251

FIG. 5. [50x482]phase transition is irreversible within the decompression [50x518]lines toward lower 2θ angles indicates a progressive relaxation [50x557]-Ga2O3 structure, as shown in Fig. 3 [50x557]/H9251

FIG. 4. The evolution of wight percent for [50x458]refinements of the diffraction patterns of [50x458]/H9251

=12.4743 Å at ambient pressure, respectively. The am-

Table I presents onset pressures of [50x374]/H9252

Table

a Å at ambient pressure, respectively. The am-

FIG. 5. (Color online) Full profile Rietveld refinements of diffraction pat-

terns for α-Ga2O3; (a) at 64.9 GPa and (b) ambient pressure. Asterisks, upper, and lower solid lines represent experimental, calculated, and differ-

cence pattern, respectively. Bars are marked at the positions of diffraction peaks.

transition in our work and others. We found that the pressure-

induced phase transition for freestanding β-Ga2O3 nanocrystal began within 13.6–16.4 GPa, higher than the previous result of 6 GPa for nanocrystalline β-Ga2O3 embedded in amorphous matrix. [21] It indicated that the host glass matrix could promote the occurrence of the β- to α-Ga2O3 phase transition. The glass matrix would introduce the anisotropic stress on the nanocrystalline β-Ga2O3 embedded in it. The anisotropic stress is supposed to play an important role in the β- to α-Ga2O3 phase transition. It was also proved by the Lipinska-Kalita et al., [16] who found that the transition pressure was 3 GPa without transmitting medium, lower than 6.5–7 GPa with nitrogen as a pressure medium. In addition, the pressure-induced coordination change and densification of the host glass matrix could also influence the phase transition, as mentioned in Ref. [21].

As to onset pressure of bulk β- to α-Ga2O3 transition, experimental data reported in recent years can be divided into two ranges of 3.3–7 and 20–22 GPa, respectively (Table I). Our result just exists between these two ranges. Thus it is difficult to judge the influence of grain size on the transition pressure. Jamieson [26] founded a relationship between transition pressure \( P_{tr} \) and energy band gap at ambient pressure \( E_g \) for semiconductors: \( P_{tr}\Delta V = E_g \), where \( \Delta V \) is the volume deviation between two phases at \( P_{tr} \). From transmission spectrum collected at ambient condition (Fig. 6), we obtained the band gap of 14 nm β-Ga2O3 as 5.9 eV, which is higher than 4.9 eV for bulk β-Ga2O3. By substituting \( E_g \) and \( \Delta V \) of bulk and nanocrystalline β-Ga2O3 into Jamieson’s function, it is deduced that the transition pressure \( P_{tr} \) for the nanocrystalline sample is higher than that for the bulk one. Based on this analysis as well as theoretical calculation results of 2.6–9 GPa for the phase transition pressure of β- to α-Ga2O3 (Table I), it is more reasonable to consider the onset pressure of phase transition for bulk sample in the range of 3.3–7 GPa. Therefore, we can conclude that the phase transition pressure of freestanding nanocrystalline β-Ga2O3 is higher than that of bulk material, consistent with the results of other nanocrystalline materials. [27–30]

The evolution of the lattice parameters with pressure for β-Ga2O3 and α-Ga2O3 is presented in Fig. 7, and the linear compressibilities are summarized in Table II. The lattice compression of both gallium oxide phases is anisotropic, with the \( a \) and \( b \) axes more compressible than the \( c \) axis in the monoclinic β-Ga2O3 structure, and with the \( c \) axis more compressible than the \( a \) axis in the rhombohedral α-Ga2O3 structure. The monoclinic angle decreased with increasing pressure, in agreement with the tendency in Ref. [15]. The compressibility values along the \( b \) and \( c \) axes of β-Ga2O3 in our study are comparable with those obtained previously for bulk β-Ga2O3 (Ref. [15]) and for nanocrystalline samples embedded in amorphous silica. [21] However, the \( a \) axis compression is only comparable with that of bulk β-Ga2O3, [15] while twice as large as that of nanocrystalline samples embedded in amorphous silica. Such difference in compressibility along the \( a \) axis might be explained by the possibility that host glass matrix surrounding the β-Ga2O3 nanocrystal could accommodate and relax the strains. The ratio of \( c/a \) for the
TABLE I. Comparison of bulk modulus $B_0$ and unit-cell volume $V_0$ of $\beta$-Ga$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ at ambient conditions, and onset pressure of $\beta$-to $\alpha$-Ga$_2$O$_3$ transition in our study with those reported.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Beginning of phase transition ($\lambda$)</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
<th>$V_0$ ($\AA^3$)</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
<th>$V_0$ ($\AA^3$)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 nm$^a$</td>
<td>13.6–16.4 GPa</td>
<td>193(6)</td>
<td>9.8(9)</td>
<td>207.0(8)</td>
<td>354(22)</td>
<td>3.0(4)</td>
<td>287.0(7)</td>
<td>ADX</td>
</tr>
<tr>
<td>14.8 nm$^b$</td>
<td>6 GPa</td>
<td>191(5)</td>
<td>8.3(9)</td>
<td>209.5(3)</td>
<td>333(19)</td>
<td>4.4</td>
<td>287.0(7)</td>
<td>EDX</td>
</tr>
<tr>
<td>Bulk$^c$</td>
<td>6.5–7 GPa</td>
<td>199(6)</td>
<td>3.1(4)</td>
<td>209.1(2)</td>
<td>220(9)</td>
<td>5.9(6)</td>
<td>288(1)</td>
<td>ADX</td>
</tr>
<tr>
<td>Bulk$^d$</td>
<td>3.3 GPa</td>
<td>184(3)</td>
<td>4.0</td>
<td>209.4(2)</td>
<td>252(14)</td>
<td>4.0</td>
<td>288(1.5)</td>
<td>ADX</td>
</tr>
<tr>
<td>Bulk$^e$</td>
<td>7.6 GPa, 1500 K</td>
<td>255(16)</td>
<td>7.6(9)</td>
<td>209.9(4)</td>
<td>261(20)</td>
<td>7.9(3)</td>
<td>288.8(1)</td>
<td>ADX</td>
</tr>
<tr>
<td>Bulk$^f$</td>
<td>20–22 GPa</td>
<td>154(12)</td>
<td>4.0</td>
<td>209.24</td>
<td>223(2)</td>
<td>4.0</td>
<td>288.96(24)</td>
<td>ADX</td>
</tr>
<tr>
<td>Bulk$^g$</td>
<td>9.5</td>
<td>142(4)</td>
<td>4.1</td>
<td>204.56</td>
<td>243</td>
<td>4.0</td>
<td>283.44</td>
<td>DFT</td>
</tr>
<tr>
<td>Bulk$^h$</td>
<td>2.6 or 6 GPa</td>
<td>202(7)</td>
<td>2.4(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ADX</td>
</tr>
</tbody>
</table>

$^a$Reference 15.
$^b$Reference 19.
$^c$Reference 18.
$^d$Reference 17.
$^e$Reference 16.
$^f$Reference 21.
$^g$Reference 17.
$^h$Reference 20.

$\alpha$-Ga$_2$O$_3$ linearly decreased during compression and then increased from 2.609 at 64.9 GPa to 2.696 at ambient pressure during decompression.

As shown in Table I, the bulk modulus of 14 nm $\beta$-Ga$_2$O$_3$ in our work is close to that of nanocrystalline sample embedded in glass matrix and slightly higher than...
TABLE II. Comparison of linear compressibilities of $\beta$-Ga$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ in our study with data reported.

<table>
<thead>
<tr>
<th>Linear compressibility</th>
<th>14 nm$^a$</th>
<th>14.8 nm$^b$</th>
<th>Bulk$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_0$ (GPa$^{-1}$)</td>
<td>6.2(5) $\times$ 10$^{-4}$</td>
<td>1.78(7) $\times$ 10$^{-3}$</td>
<td>8.2 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>$\beta_0$ (GPa)</td>
<td>1.30(6) $\times$ 10$^{-3}$</td>
<td>1.97 $\times$ 10$^{-3}$</td>
<td>1.45(2) $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>$\beta_0$ (GPa$^{-1}$)</td>
<td>1.10(3) $\times$ 10$^{-3}$</td>
<td>9.34(9) $\times$ 10$^{-4}$</td>
<td>8.8 $\times$ 10$^{-4}$</td>
</tr>
</tbody>
</table>

$^a$This study.
$^b$Reference 21.
$^c$Reference 15.

that of bulk $\beta$-Ga$_2$O$_3$, while bulk modulus of $\alpha$-Ga$_2$O$_3$ in our work is much higher than that of the bulk material which might be connected with the high surface energy of $\alpha$-Ga$_2$O$_3$. Further investigation is required to get a better understanding of this elevation.

IV. CONCLUSIONS

The high-pressure behavior of 14 nm $\beta$-Ga$_2$O$_3$ particles was investigated using angle-dispersive synchrotron XRD up to 64.9 GPa. It was found that the onset transition pressure of $\beta$- to $\alpha$-Ga$_2$O$_3$ was within 13.6–16.4 GPa, and phase transition was sluggish and irreversible with $\alpha$-Ga$_2$O$_3$, remaining after pressure release. Based on the first principles calculations reported and the relationship between the transition pressure and energy gap, we conclude that the transition pressure of nanocrystalline $\beta$-Ga$_2$O$_3$ is higher than that of bulk counterpart. According to the hydrostatic compression data, the bulk modulus at a fixed $B_0^\prime$ = 4 of nanocrystalline $\beta$-Ga$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ was estimated at 228(9) GPa and 333(19) GPa, both higher than the bulk materials, respectively.

FIG. 8. (Color online) The evolution of $V/V_0$ for $\beta$-Ga$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ with pressure. Solid lines and dashed lines are the Birch–Murnaghan equation of state fits to experimental data with unfixed $B_0^\prime$, and with fixed $B_0^\prime$ = 4, respectively.

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