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High-pressure behavior of β -Ga₂O₃ nanocrystals

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Freestanding nanocrystalline β -Ga₂O₃ 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 β -Ga₂O₃ underwent a phase transition to rhombohedral α -Ga₂O₃. It was found that β - to α -Ga₂O₃ transition began at about 13.6–16.4 GPa, and extended up to 39.2 GPa. At the highest pressure used, only α -Ga₂O₃ was present, which remained after pressure release. A Birch–Murnaghan fit to the P - V data yielded a zero-pressure bulk modulus at fixed $B'_0=4$: $B_0=228(9)$ GPa and $B_0=333(19)$ GPa for β -Ga₂O₃ and α -Ga₂O₃ phases, respectively. We compared our results with bulk β -Ga₂O₃, and concluded that the phase-transition pressure and bulk modulus of nanocrystalline β -Ga₂O₃ are higher than those of bulk counterpart.

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I. INTRODUCTION

Monoclinic gallium oxide (β -Ga₂O₃), 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 application.^{1–5} Recently, considerable effort has been devoted to the study of nanostructured β -Ga₂O₃ because of the potential for applications in nanodevices.^{6–10} In ambient conditions, monoclinic β -Ga₂O₃ is the thermodynamically stable form and there are other four metastable structures: α -, γ -, δ -, and ϵ -Ga₂O₃.¹¹ Different forms have different physical properties. For example, the band gap of the α -Ga₂O₃ polymorph is 2.41 eV, much narrower than that of β -Ga₂O₃.¹² So it is important to clarify the relationship between different structures, which can be accessed by research on high-pressure phase transition. Especially for nanocrystal materials, investigation of the high-pressure behavior reveals the contribution of boundary in phase transition and provides additional insights into size-dependent changes in phase stability and mechanical properties.

The high-pressure behavior of β -Ga₂O₃ had not received much attention until recently.^{13–21} It is verified that β -Ga₂O₃ undergoes a sluggish transition to α -Ga₂O₃ under high pressure. However, there is still a controversy on the value of the transition pressure. Machon *et al.*¹⁵ indicated that β - to α -Ga₂O₃ phase transition occurred at 20–22 GPa, while Lipinska-Kalita *et al.*¹⁶ found that transition began at 6.5–7 GPa at ambient temperature. Theoretical calculations based on density-functional theory gave the transition pressure of 2.6 GPa (Ref. 18) when the d electron of Ga was treated as core state, and of 6 GPa (Ref. 18) and 9.5 GPa (Ref. 19)

when the d electron of Ga as valence state. Lipinska-Kalita *et al.*¹⁶ also reported that the transition pressure with and without transmitting medium were 6.5–7 and 3 GPa, respectively.

Research on high-pressure phase transition of nanocrystalline β -Ga₂O₃ can only be found in the work of Lipinska-Kalita *et al.*²¹ They reported the β - to α -Ga₂O₃ transition, beginning at 6 GPa, in nanocrystalline β -Ga₂O₃ 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 β -Ga₂O₃, or are promoted by anomalous densification among the silica matrix. These results encourage us to re-examine the high-pressure behavior of freestanding β -Ga₂O₃ nanoparticles by angle-dispersive x-ray diffraction (XRD) technique.

II. EXPERIMENTS

Monoclinic β -Ga₂O₃ nanoparticles were synthesized as follows: 0.7 g GaCl₃, 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 °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 °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 °C. The average crystallite size of Ga₂O₃ 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 β -Ga₂O₃ were performed at beam line BL-13A in High Energy Accelerator Research Organization (KEK).

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FIG. 1. (Color online) Full profile Rietveld refinement of diffraction pattern for nanocrystalline β -Ga₂O₃. Asterisks, upper, and lower solid lines represent experimental, calculated, and difference pattern, respectively. Bars are marked at the positions of diffraction peaks.

Monochromatic x-ray ($\lambda=0.42713$ Å) was collimated to 50×50 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 Ga₂O₃ nanoparticles which was used to identify the structure and to estimate the mean grain size. A Rietveld full profile refinement²⁵ confirmed that all the peaks in the XRD pattern corresponded to the monoclinic β -Ga₂O₃ (space group $C2/m$). No peaks of any other phases were detected. The refined β -Ga₂O₃ 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 $V=209.51(4)$ Å³, 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 $V=209.56(4)$ Å³].¹⁶ The average grain size of nanocrystalline β -Ga₂O₃ 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 -Ga₂O₃ 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

FIG. 2. Transmission electron microscopic patterns of nanocrystalline β -Ga₂O₃: (a) low magnification image and (b) HRTEM image.

FIG. 3. Selected angle-dispersive synchrotron XRD patterns: (a) compression up to 64.9 GPa and (b) subsequent decompression. The appearance of the (113) peak for α -Ga₂O₃ is arrowed.

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 -Ga₂O₃ 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 -Ga₂O₃, in accordance with former results.^{15,16,21}

At the beginning of phase transition, the (104) and (110) peaks, two strong reflections of α -Ga₂O₃, were overlapped with the ($\bar{1}11$) and (111) peaks of the still dominating β -Ga₂O₃, 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 -Ga₂O₃ 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 -Ga₂O₃ and α -Ga₂O₃ with pressure is presented in Fig. 4. It is clearly shown that the weight percent of β -Ga₂O₃ keeps close to 100% below 13.6 GPa. For the pattern at 16.4 GPa, the Rietveld refinement confirmed that β - and α -Ga₂O₃ 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 -Ga₂O₃ was the dominating phase up to 19.8 GPa, and tiny β -Ga₂O₃ 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 Ga₂O₃.¹⁶

All patterns collected from the decompression sequence only attribute to α -Ga₂O₃, and the gradual shift of diffraction

FIG. 4. The evolution of weight percent for β -Ga₂O₃ and α -Ga₂O₃ with pressure during compression.

lines toward lower 2θ angles indicates a progressive relaxation of the α -Ga₂O₃ structure, as shown in Fig. 3(b). That demonstrates the pressure-driven β - to α -Ga₂O₃ phase transition is irreversible within the decompression time scale used here. Figure 5 illustrates Rietveld full profile refinements of the diffraction patterns of α -Ga₂O₃ at 64.9 GPa and ambient pressure. The refinements yielded the following lattice parameters of α -Ga₂O₃: $a=4.7807(9)$ Å, $c=12.4743(29)$ Å at 64.9 GPa and $a=4.9723(6)$ Å, $c=13.4031(17)$ Å at ambient pressure, respectively. The ambient lattice parameters of α -Ga₂O₃ correspond well with the results of Lipinska-Kalita *et al.*¹⁶ [$a=4.979(10)$ Å and $c=13.432(28)$ Å].

Table I presents onset pressures of β - to α -Ga₂O₃ phase

FIG. 5. (Color online) Full profile Rietveld refinements of diffraction patterns for α -Ga₂O₃: (a) at 64.9 GPa and (b) ambient pressure. Asterisks, upper, and lower solid lines represent experimental, calculated, and difference 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. Jamieson²⁶ founded a relationship between transition pressure P_{tr} and energy band gap at ambient pressure E_g for semiconductors: $P_{tr}\Delta V \propto E_g$, where ΔV 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 ΔV 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 β -Ga₂O₃ and α -Ga₂O₃ at ambient conditions, and onset pressure of β -to α -Ga₂O₃ transition in our study with those reported.

Sample	Beginning of phase transition	β -Ga ₂ O ₃			α -Ga ₂ O ₃			Method
		B_0 (GPa)	B'_0	V_0 (Å ³)	B_0 (GPa)	B'_0	V_0 (Å ³)	
14 nm ^a	13.6–16.4 GPa	193(6)	9.8(9)	207.0(8)	354(22)	3.0(4)	287.0(7)	ADX
		228(9)	4	207.0(8)	333(19)	4	287.0(7)	
14.8 nm ^b	6 GPa	191(5)	8.3(9)	209.5(3)				EDX
Bulk ^c	6.5–7 GPa	199(6)	3.1(4)	209.1(2)	220(9)	5.9(6)	288(1)	ADX
		184(3)	4	209.4(2)	252(14)	4	288(1.5)	
	3.3 GPa	255(16)	7.63(90)	209.9(4)	261(20)	7.93(71)	288.8(1)	
Bulk ^d	7.6 GPa, 1500 K	134(12)	4	209.24	223(2)	4	288.96(24)	ADX
		142	4.1	204.56	243	4.0	283.44	DFT
Bulk ^e	20–22 GPa	202(7)	2.4(6)					ADX
Bulk ^f	9.5	174	3.79		210	4.95		DFT
Bulk ^g	2.6 or 6 GPa							DFT

^aThis study.^bReference 21.^cReference 16.^dReference 17.^eReference 15.^fReference 19.^gReference 18.

α -Ga₂O₃ linearly decreased during compression and then increased from 2.609 at 64.9 GPa to 2.696 at ambient pressure during decompression.

The V/V_0 relations as a function of pressure for nanocrystalline β -Ga₂O₃ and α -Ga₂O₃ during compression are shown in Fig. 8. At 16.4 GPa, the volume collapse across the phase transition was about 6.5%. The P - V data were fitted using a third-order Birch–Murnaghan equation of state

$$P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}] \times \{1 + 0.75(B'_0 - 4) \times [(V/V_0)^{-2/3} - 1]\},$$

where V_0 is the volume at ambient pressure, B_0 is the bulk modulus at ambient pressure, and B'_0 is the pressure derivative at ambient pressure. The fitting parameters B_0 and B'_0 are summarized in Table I, where reported data are also presented. Since the value of B'_0 differs largely between the two phases, we fitted again the compression data by fixing $B'_0 = 4$ to give a better idea of the relative compressibility between β -Ga₂O₃ and α -Ga₂O₃ phases. It should be pointed out that the data of minor phase while two phases coexist, α -Ga₂O₃ phase at low pressure and β -Ga₂O₃ phase at high pressure, were not fitted because of their large uncertainty.

FIG. 6. The optical transmission spectrum of 14 nm β -Ga₂O₃ at ambient condition.

As shown in Table I, the bulk modulus of 14 nm β -Ga₂O₃ in our work is close to that of nanocrystalline sample embedded in glass matrix and slightly higher than

FIG. 7. (Color online) Pressure evolution of lattice parameters: (a) of the β -Ga₂O₃, and (b) of the α -Ga₂O₃. Solid and open symbols refer to the compression and decompression data, respectively. The differential (in angstrom) of the vertical scales of each graph is the same, in order to facilitate comparison between the evolutions of lattice parameters. Dot lines are drawn as a guide for the eyes.

TABLE II. Comparison of linear compressibilities of β -Ga₂O₃ and α -Ga₂O₃ in our study with data reported.

Linear compressibility	14 nm ^a		14.8 nm ^b	Bulk ^c
	α -Ga ₂ O ₃	β -Ga ₂ O ₃	β -Ga ₂ O ₃	β -Ga ₂ O ₃
β_a (GPa ⁻¹)	$6.21(5) \times 10^{-4}$	$1.78(7) \times 10^{-3}$	8.2×10^{-4}	$1.99(9) \times 10^{-3}$
β_b (GPa ⁻¹)		$1.30(6) \times 10^{-3}$	1.97×10^{-3}	$1.45(2) \times 10^{-3}$
β_c (GPa ⁻¹)	$1.10(3) \times 10^{-3}$	$9.34(9) \times 10^{-4}$	8.8×10^{-4}	$8.8(4) \times 10^{-4}$

^aThis study.^bReference 21.^cReference 15.

that of bulk β -Ga₂O₃, while bulk modulus of α -Ga₂O₃ in our work is much higher than that of the bulk material which might be connected with the high surface energy of α -Ga₂O₃. Further investigation is required to get a better understanding of this elevation.

IV. CONCLUSIONS

The high-pressure behavior of 14 nm β -Ga₂O₃ particles was investigated using angle-dispersive synchrotron XRD up to 64.9 GPa. It was found that the onset transition pressure of β - to α -Ga₂O₃ was within 13.6–16.4 GPa, and phase transition was sluggish and irreversible with α -Ga₂O₃, 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 β -Ga₂O₃ is higher than that of bulk counterpart. According to the hydrostatic compression data, the bulk modulus at a fixed $B'_0=4$ of nanocrystalline β -Ga₂O₃ and α -Ga₂O₃ 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 β -Ga₂O₃ and α -Ga₂O₃ with pressure. Solid lines and dashed lines are the Birch–Murnaghan equation of state fits to experimental data with unfixed B'_0 , and with fixed $B'_0=4$, respectively.

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