High pressure Raman spectrum study of Ga_2O_3

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Abstract

In-situ high-pressure Raman study and X-ray diffraction of *β*-Ga_2O_3 has been carried out from 0 to 16 GPa at room temperature with a gasketed diamond anvil cell. All Raman frequencies continuously increase with increasing pressure. The ten expected Raman active phonons were found and their symmetry characters determined. It has not been found that the pressure-induced phase transition occurred.

Keywords: Raman spectroscopy high pressure Ga_2O_3 X-ray diffraction

1. Introduction

Monoclinic gallium oxide (*β*- Ga_2O_3) is an important wide band gap (*E*g = 4.9 eV) material because of good chemical and thermal stability(1). It has great potential application in optoelectronic nanodevices and gas sensors，so much attention has recently been given the synthesis of single-crystalline *β*- Ga_2O_3 nanoribbons，nanosheets and nanowires. Till now，many methods are available for synthesis of single-crystalline *β*- Ga_2O_3(2-5). However，high pressure behavior of *β*-Ga_2O_3 is less investigated. The transformation from *β*-Ga_2O_3 to *α*-Ga_2O_3 (trigonal) under high temperature(1000℃) and high pressure(44Kbar) conditions was first reported by Remeika(9) in 1966. High pressure Raman behavior of *β*-Ga_2O_3 have never been reported.

Gallium oxide crystal have much forms—*α β γ δ* and *ε*- Ga_2O_3，in the literature have been given the conditions under which these structures appear(6) .Thereinto，the most stable and familiar one is *β*- Ga_2O_3，the melting point is 1715°(4). In *β*-Ga_2O_3 (*a*=12.23 Å，*b*=3.04 Å，*c*=5.580 Å，*α*=90°，*β*=103.7°，*γ*=90°，space group，C2/m) there are two kinds of coordination for the gallium ions，namely tetrahedral and octahedral and 4 Ga_2O_3 in the unit cell(7).In *α*-Ga2O3，which is isostructural with *α*-corundum, the gallium ions have coordination number 6 only. The lattice parameters are *a*=4.9825 Å，*c* =13.433 Å，there are 6 Ga_2O_3 in the unit cell(8).

In this work we have explored vibrational properties of *β*-Ga_2O_3 at ambient and high pressure using Raman spectroscopy. Raman experiments have been complemented with X-ray diffraction measurements in a diamond anvil cell.

2. Experimental

The experimental sample is white powders of pure gallium oxide. The XRD results under ambient pressure and temperature show that the sample is an *β*-Ga_2O_3 crystal. We conduct a high-pressure experiment by using a diamond-anvil-cell(DAC).The samples(approximately 10-30μm) were loaded into the hole(200μm in diameter and 60-80μm in depth) in a hardened stainless steel

gasket in DAC .The anvil faces are 500μm in diameter. Fine powders of ruby were also placed inside the hole，and ethanol-methanol(4:1) mixture was used as pressure-transmitting medium. The sample crystals were set on top of ruby powder. The hydrostatic condition has been attained at a pressure above 10GPa. Pressures were measured using the ruby-fluorescence technique.

The Raman spectrum was recorded with a T64000 with liquid-N2-cooled CCD detector in a backscattering geometry at room temperature. The spectra were excited by the 488 nm line of an Ar^+ laser focused down to a 7μm spot on the sample. The laser power was low enough to avoid heating of the sample. The range of frequencies for Raman spectra was 100—1000cm^{-1}.Peaks were fitted using the Origin computer software.

The high pressure X-ray diffraction patterns were recorded in an energy dispersive configuration in the Institute of High Energy Physics, Academia Sinica, in Beijing. The diffraction angle 2θ=15.89°, the range of energies is 5~35KeV. Powdered β-Ga_2O_3 was loaded in the 150μm hole of a hardened stainless steel gasket .The anvil faces are 500μm in diameter. Pressure in the diamond-anvil cell was measured by the shift of ruby fluorescence R_1 line， and ethanol-methanol (4:1) mixture was used as pressure-transmitting medium.

3. Results and discussion

Raman spectra of the β-Ga_2O_3 at high pressure are shown at Fig.1. Ten Raman modes have been observed，there are modes at 144，169，199，320，346，415，475，629，655 and 766 cm^{-1}，respectively. The corresponding symmetries and assignments are listed in Table1.According to factor group analysis，the crystal modes can be classified:

$$\Gamma_{vib} = 10A_g + 5B_g + 10B_u + 5A_u$$

where A_u,$2B_u$ modes are acoustic modes, a total of 15 Raman modes and 12 infrared active modes are predicted for β- Ga_2O_3[11] .

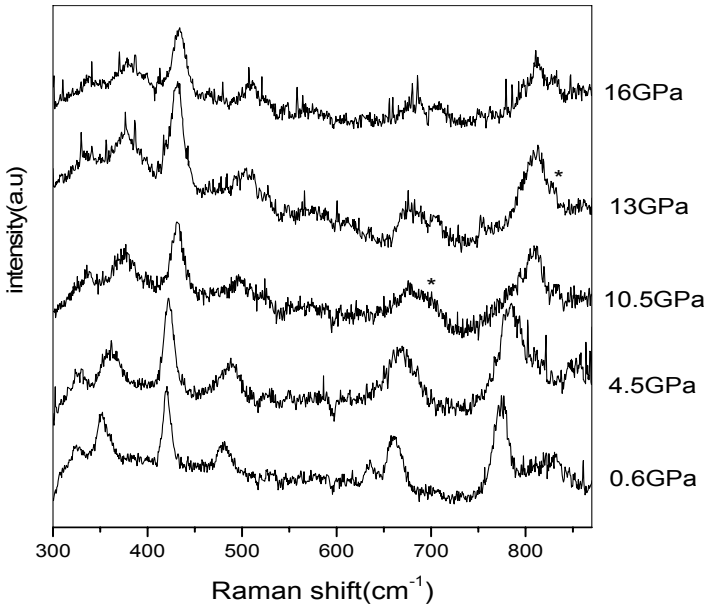

Fig.1. Raman spectra of β- Ga_2O_3 as a function of pressure at room temperature. The asterisks indicate the new bands.

The spectrum is dominated by a strong peak at 199cm^{-1}, this mode derived from the librations of chains around the *y* axis. The bands at lower frequencies are assigned to the librations and translations of chains. The bands at 415, 346，318 cm^{-1} are assigned to the deformation of octahedron. The bands at 766, 655，629，475 cm^{-1} derived from the stretching and bending of tetrahedron.

Table1.Ambient frequencies(cm^{-1}) of Raman modes of β-Ga_2O_3 and symmetries and assignments[11]

Raman shift(cm^{-1})	Assignment	Symmetries
766	γ_3	A_g
655	γ_3	A_g
629	γ_1	A_g
475	γ_4	B_g
415	γ_2	A_g
346	γ_2	A_g
320	γ_2	A_g
199	L	A_g
169	T	A_g
144	T	B_g

γ_1 symmetric stretching of tetrahedron; γ_3 asymmetric stretching of tetrahedron; γ_4 bending of tetrahedron ; γ_2 deformation of octahedron; L libration; T translation

The number of observed bands in the Raman spectrum of β-Ga_2O_3 at ambient pressure is smaller than that inferred from factor group analysis，The ten expected Raman active phonons were found and their symmetry characters determined，the lack of Raman bands in β-Ga_2O_3 is chiefly attributed to weak intensity of signals.

The pressure dependence of the Raman frequencies of β- Ga_2O_3 was studied up to 16Gpa at room temperature (Fig.2). All the Raman frequencies of β- Ga_2O_3 increase with increasing pressure. The 629cm^{-1} mode increases faster in frequency with increasing pressure than the 655 cm^{-1}mode.This leads to a merging of the two bands under compression, resulting in a complete overlap at pressure above 4.5Gpa.At pressure above 10.5GPa the 655cm^{-1} band splits into two bands, similarly to the 766cm^{-1} band also splits into two bands at 13GPa. with increasing pressure，and the split linewidth increase also. Presumably crystal lattice occurred distortion because these vibrations are asymmetric internal modes. To clarify this point, we present X-ray diffraction data.

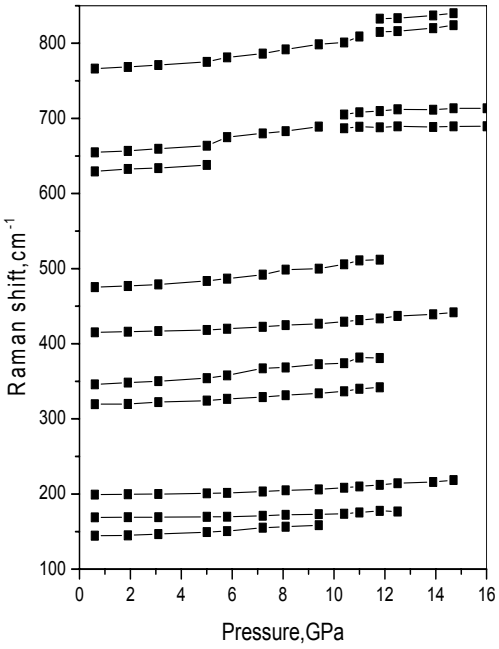

Fig.2.Pressure dependences of the Raman bands

In situ X-ray diffraction patterns were recorded up to 23GPa(Fig.3). We do not observe evidence for the occurrence of a phase transition within the range of conditions investigated. At pressure about 15.2GPa, a new peak appeared, this is chiefly attributed to random distribution in the orientation of crystals(Fig.4).Accoding to Tu[12], structural changes from the β-Ga_2O_3 structure into the α-Ga_2O_3 structure occurred. This argument is not consistent with our results. The pressure dependence of the weak bands in the 160–350cm^{-1} region indicates that phase transition did not occur, marked by no an abrupt change in their frequencies.

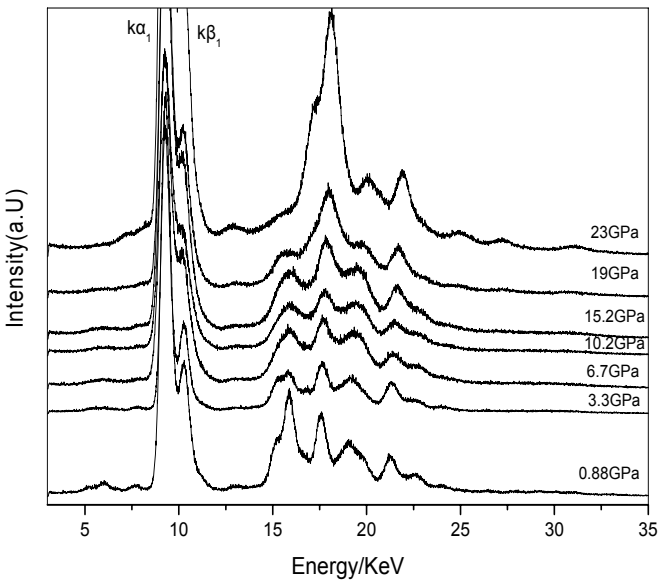

Fig.3. XRD patterns of β- Ga_2O_3 as function of pressure. Kα and kβ_1 are the X-ray emission lines of Ga.

The transformation from β-Ga_2O_3 to α-Ga_2O_3 (trigonal) under high temperature(1000℃) and high pressure(44Kbar) conditions was first reported by Remeika[9] in 1966. But we do not observe evidence for the occurrence of a phase transition.

4. Conclusion

In summary，we studied high pressure Raman behavior of β-Ga_2O_3 in a diamond-anvil cell，and explored vibrational properties of β-Ga2O3 at ambient and high pressure. It has not been found that the pressure-induced phase transition occurred within the range of conditions investigated.

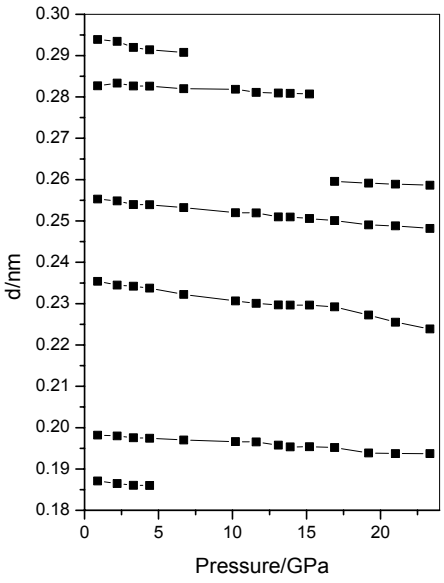

Fig.4. Pressure dependence of X-ray peaks

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