Experimental Observation of Phase Transition in Sb_2O_3 under High Pressure *

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The in situ high-pressure behavior of the semiconductor antimony trioxide (Sb_2O_3) is investigated by the Raman spectroscopy techniques and angle-dispersive synchrotron x-ray powder diffraction in a diamond anvil cell up to 31.5 and 30.7 GPa, respectively. New peaks observed in the external lattice mode range in the Raman spectra at 13.5 GPa suggest that the structural phase transition occurs. The group mode (140 cm^{-1}) in Sb_2O_3 exhibits anomalous pressure dependence; that is, the frequency decreases gradually with the increasing pressure. High pressure synchrotron x-ray diffraction measurements at room temperature reveal that the transition from the orthorhombic structure to high-pressure new phase occurs at about 14.2 GPa, corresponding to the softening of the group optic mode (140 cm^{-1}).

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Antimony trioxide (Sb_2O_3) is a transparent material with an indirect band gap of 3.3 eV that has been widely used in catalysis, fire retardants, glasses, sensors, as anode material for the Li-ion batteries, and retardants for rubber, ceramics, enamels, fabrics, and fiber products.[1−7] Moreover, the Sb_2O_3 thin film behaves as an n-type semiconductor,[8] which invites its photovoltaic applications. Sb_2O_3 exists mainly in two crystalline forms, namely the cubic senarmontite form and the orthorhombic valentinite.[9] Senarmontite (cubic Sb_2O_3) is stable phase at low temperature $T < 570$ K and has a structure based on Sb_4O_6 molecules, in which SbO_3(E) pyramids are linked at their corners to form a cage-like structure (E being lone pair of electrons); and valentinite (orthorhombic Sb_2O_3) is high temperature phase stable above 570 K and also consists of SbO_3(E) pyramids, and has a double chain structure consisting of four membered rings of pyramids.[9,10]

Recent research on Sb_2O_3 has focused on the synthesis and preparation of nanoparticles[11−16] such as nano-spheres, nano-wires, nanobelts and nanorods[17−21] due to the applications in the manufacture of advanced nanodevices. However, very few reports are available[10,22−25] regarding the Raman studies of Sb_2O_3 either in the nano-material form or in the bulk form. Mestl *et al.*[9] have investigated the spectroscopic behavior of Sb_2O_3/Sb_2O_4 in oxidizing and reducing atmospheres. Gilliam *et al.*[25] have carried out the first ab initio theoretical study of tetraantimony hexoxide (Sb_4O_6). They calculated the normal mode frequencies, intensities, and the corresponding vibrational assignments of Sb_4O_6 in T_d symmetry. However, we have not yet found reports of high-pressure behavior on orthorhombic Sb_2O_3. In fact, the pressure plays an important role in the study of semiconductors.[26−28] Even modest pressures of 1–2 GPa can induce significant change in the crystal and electronic structures of semiconductors. This work presents the in-situ Raman spectroscopy and x-ray diffraction measurements of orthorhombic valentinite Sb_2O_3 up to pressures of 31.5 and 30.7 GPa, respectively. The band at 140 cm^{-1} (assigned to group mode) has a pressure dependence of -0.369 cm^{-1}/GPa below the pressure of 13.5 GPa and reveals significant softening at high pressure. A reversible structural transformation of Sb_2O_3 was observed at 13.5 GPa.

Commercially available orthorhombic valentinite Sb_2O_3 powder (99%) was used. For the high pressure experiments, the sample was finely ground and loaded into a diamond-anvil cell with anvil faces diameter of 500 μm together with a small chip of ruby. A T301 stainless steel gasket was preindented to a thickness of 80 μm and a 200 μm hole was drilled in the center of the preindented area. The pressure-transmitting medium was a mixture of ethanol-methanol-water (16:3:1). The pressure was calibrated by the well-known ruby fluorescence method.[29] In situ high-pressure angle-dispersive x-ray diffraction (ADXRD) experiments were carried out at BL15U1 beamline of the Shanghai synchrotron radiation facility (SSRF). The monochromatic beam wavelength used for data collection was 0.6199 Å with a 2×3 μm^2 size. Diffraction images were collected by using an MAR-165 charge-coupled device (CCD) de-

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tector. The Bragg diffraction rings were recorded with an imaging plate detector, and the two-dimensional XRD images were analyzed by using FIT2D software, yielding one-dimensional intensity versus diffraction angle 2 patterns.[30] The Raman spectra were recorded at room temperature by a Renishaw-1000 Raman using the 532 nm line of solid state laser as the excitation source. The scattered light was collected in backscattering geometry.

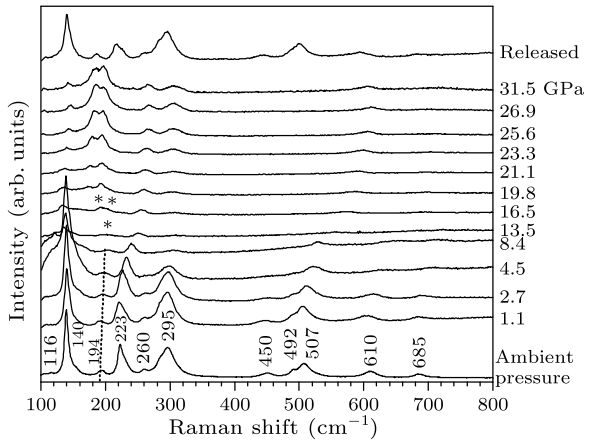

Fig. 1. Selected Raman spectra of Sb_2O_3 as a function of pressure at room temperature. The stars indicate bands of new phase which appear at a pressure of 13.5 GPa. The dashed line indicates that the band at 194 cm^{-1} at ambient pressure gradually disappears with the increasing pressure. The top pattern is a Raman spectrum at ambient pressure after decompressing from 31.5 GPa.

Sb_2O_3, as important V–VI group semiconductors materials, have attracted a great deal of attention with regard to their thermoelectric effects and structural properties. Raman spectroscopy has been known to be one of the most convenient and powerful tools to study structural characters of materials through the solid-state effects on dynamical properties. It provides valuable information on local and cooperative changes during pressure-related transformations between phases. Orthorhombic form Sb_2O_3 can be considered to consist of four SbO_3 (E) pyramids (E being lone pair of electrons) arranged into the Sb_4O_6 molecular ring structure with a T_d symmetry.[10,25] Each oxygen is bridged between two SbO_3 pyramids. Gilliam *et al.*[25] gave the decomposition of the reducible representation of the vibrational degrees of freedom with the T_d point group,

$$\Gamma_{\rm vib} = 2A_1 + 2E + 2T_1 + 4T_2,$$

where A_1, E and T_2 are the Raman active modes. Figure 1 shows some representative Raman spectra of Sb_2O_3 in the frequency range of 100–800 cm^{-1} at different pressures. At ambient conditions (on the bottom in Fig. 1), the position of Raman peaks observed are in good agreement with the other works published,[20–23] which is a characteristic of the orthorhombic valentinite form of Sb_2O_3. All signals below 400 cm^{-1} belong to the external lattice mode, which is controlled by the crystal space group and unit cell coupling. Those signals above 400 cm^{-1}, in the internal mode region (400–800 cm^{-1}), is mainly controlled by the spectral features of polymeric Sb–O chains.[22] The internal modes are further classified into symmetric (v_s) and asymmetric (v_{as}), stretching modes at 685 and 610 cm^{-1} in addition to the symmetric δ_s and asymmetric δ_{as}, bending modes located 507 and 450 cm^{-1},[10] respectively.

During the compression study, the Raman spectrum contained only the features assigned to orthorhombic valentinite form of Sb_2O_3 up to pressure of 0–13.5 GPa (Fig. 1). At pressures higher than 13.5 GPa, new bands start to appear in the low frequency range (marked with stars in Fig. 1). These bands show a pressure-induced increase in intensity and shift, and simultaneously the bands assigned to the orthorhombic Sb_2O_3 weaken and disappear gradually. For example, the strongest Raman band of the orthorhombic form Sb_2O_3 near 140 cm^{-1} is only just visible in the spectrum at 13.5 GPa. The dashed line in Fig. 1 also indicates that the band at 194 cm^{-1} gradually disappears with the increasing pressure. These Raman features at high pressures suggest that a structural phase transition has been obtained at 13.5 GPa in Sb_2O_3 from orthorhombic structure to high-pressure new phase at room temperature.

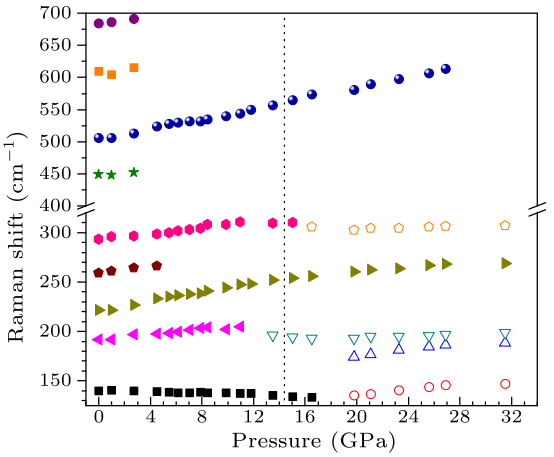

Fig. 2. Pressure dependence of Raman modes of Sb_2O_3 during compression from 0 to 31.5 GPa. Open symbols represent new Raman bands which begin to appear at 13.5 GPa.

The shifts of Raman frequencies as a function of observed pressure from 0 to 31.5 GPa are depicted in Fig. 2. We can see that most of the modes exhibit positive changes in frequency with pressure, as is expected, while the band at 140 cm^{-1} (assigned to group mode) shows a frequency decrease with the increasing pressure. It has a pressure dependence of -0.369 cm^{-1}/GPa below the pressure of 13.5 GPa and

reveals significant softening at high pressure. This mode plays an important role in the pressure-induced phase transition in Sb_2O_3. A similar pressure dependence was observed in rutile-type dioxides, the B_{1g} mode softening induced a second-order phase transition from tetragonal to orthorhombic under high pressure by the Raman spectra measurements.[31] The top pattern in Fig. 1 presents the Raman spectrum when the pressure is released to ambient environment. It has the same pattern as that of the starting material except for broader features, indicating the reversibility for the phase transition.

All of the other vibrational peaks shifted toward high frequencies and there are apparent discontinuities around 13.5 GPa on all modes (see Fig. 2). The figure shows a structural phase transition at 13.5 GPa in antimony trioxide. In addition, the average pressure derivative of the high-frequency modes (400–800 cm^{-1}) is larger than that of the low-frequency modes (smaller than 400 cm^{-1} (0–2 cm^{-1}/GPa)). The pressure dependences of the observed bands and assignments are presented in Table 1.

Table 1. Ambient Raman frequency, their pressure dependences and assignments for orthorhombic valentinite form of Sb_2O_3. Here δ_{as} is the asymmetric bending mode, δ_s is the symmetric bending mode, v_{as} is the asymmetric stretching mode, and v_s is the symmetric stretching mode.

v (cm^{-1}) Ref. [10]	v (cm^{-1}) Ref. [22]	v (cm^{-1}) This study	dv/dP (cm^{-1}/GPa)	Assignments[10]
	103			Group
		116		Group
	140	140	−0.369	Group
	194	194	1.223	Group
219	223	223	1.632	Group
256	269	260	1.536	Group
297	294	295	1.245	Group
375				Group
451	449	450	1.254	δ_{as}
			492	
502	502	507	4.032	δ_s
597	602	610	2.670	v_{as}
683	690	685	2.852	v_s
713				v_s

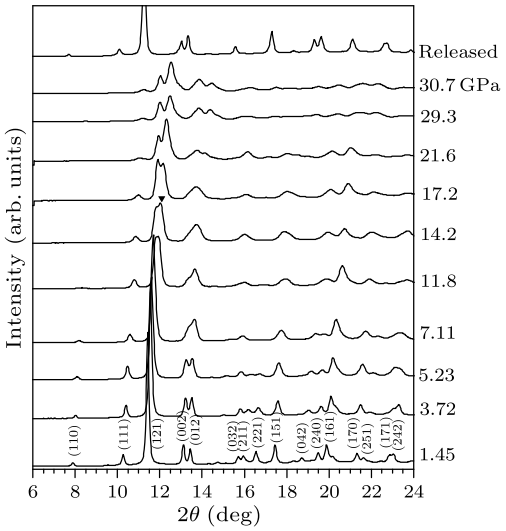

Fig. 3. XRD patterns collected at various pressures for Sb_2O_3 with incident wavelength $\lambda = 0.6199$ Å. The closed triangle shows the appearance of a new Bragg peak. The top pattern is the XRD spectrum at room pressure after releasing pressure from 30.7 GPa.

The structural phase transition of Sb_2O_3 is also studied by using in situ synchrotron x-ray diffraction at high pressures. Figure 3 shows some representative XRD patterns of Sb_2O_3 at different pressures. Under ambient conditions, all of the diffraction peaks can be indexed to a pure orthorhombic structure with space group No. 56 and lattice constants of $a = 4.91$ Å, $b = 12.46$ Å and $c = 5.41$ Å. As the pressure increases, the diffraction lines shift toward higher 2θ angles and are accompanied by a change of the relative intensities. It is clear from Fig. 3 that up to a pressure of 14.2 GPa, the new diffraction peak, which becomes gradually stronger with pressure, is indicated with a star at 14.2 GPa. Other diffraction peaks from the orthorhombic Sb_2O_3 become weaker and disappear, indicating that the orthorhombic Sb_2O_3 begins to transform to a high-pressure new phase at room temperature. The phase transition pressure observed in XRD experiments is in good agreement with the Raman data. If the phase transition in Sb_2O_3 is driven by the softening of the group mode (140 cm^{-1}) with pressure, then the transition in Sb_2O_3 may be close to the second order. The crystal structures of the high-pressure new phase have not yet been determined.

In summary, we have experimentally confirmed a pressure-induced structural phase transition of Sb_2O_3 using in situ Raman spectra and synchrotron-radiation XRD measurements up to 31.5 and 30.7 GPa, respectively. The transition at pressure of 13.5 GPa from orthorhombic structure to new structural phase corresponds to the softening of a group mode (140 cm^{-1}). The broadened bands result from the SbO_3 tetrahedra distortion. The crystal structures

of high-pressure new phase are still under investigation.

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