J Mater Sci (2007) 42:2582–2585
DOI 10.1007/s10853-006-1417-5

High pressure Raman spectroscopic study of structural phase transition in samarium oxide

Teruhisa Hongo · Ken-ichi Kondo ·
Kazutaka G. Nakamura · Toshiyuki Atou

Received: 22 August 2005 / Accepted: 9 February 2006 / Published online: 2 January 2007

Abstract High pressure Raman spectroscopic study of Sm_2O_3 poly crystal was performed up to 21.0 GPa and room temperature using a diamond anvil cell. Pressure induced phase transition was observed at 2.6 GPa in the pressure increasing process. This phase transition corresponds to the monoclinic B type phase → the hexagonal A type transformation. The A type phase was stable up to 21.0 GPa. In the pressure release process, the A type phase was stable above 1.8 GPa, and was completely reverted to the B type phase at 1.1 GPa. The phase transition was confirmed to be reversible with a hysteresis of approximately 1.0 GPa.

Introduction

The rare earth sesquioxides are known to exist in three polymorphs denoted as A, B, and C-type by Goldschmidt et al. [1]. Their stability at ambient pressure and temperature depends on radius ratio of cation and anion [2]. The oxide of larger size cations from lanthanum to neodymium forms the hexagonal A-type structure with space group $P\bar{3}m1$. An intermediate size cation from samarium to gadolinium has the monoclinic B-type structure with space group $C2/m$. The cubic C-type structure with space group $Ia\bar{3}$ is formed by other lanthanoid ions. The density of these three crystal structure increases in the order of the C, B, and A-type structure accompanied by increase in coordination number of cations, several rare earth sesquioxides with the C-type structure were reported to transform to the B-type structure under static high pressure and high temperature by quenching method [2–11]. Also, reversible B ⇔ A phase transitions were observed for Sm_2O_3 and Gd_2O_3 by in situ X-ray diffraction experiment using synchrotron radiation at room temperature [12, 13]. The transition pressure to the A-type structure was determined to be 2.5 GPa for Sm_2O_3 and 5.2 GPa for Gd_2O_3 at room temperature. Since Hyde et al. reported that a close relationship between the A- and B-type structure [14], displacive type phase transition mechanism has been inferred. To clarify the nature of this phase transition, vibrational spectroscopy using Raman scattering might be effective.

In this work, we present Raman spectroscopic study on Sm_2O_3 under high pressure and room temperature. Structural evolution of Sm_2O_3 under high pressure was followed up to 21.0 GPa by Raman spectroscopy at room temperature, and precise phase transition pressure and quantitative information on pressure variation of the Raman shift were determined.

Experimental

Chemical reagent of the B type Sm_2O_3 with purity of 99.9% was obtained from Nippon Yttrium Co., Ltd. The sample was sintered at 1,500 °C for 10 h to eliminate the impurities such as the C-type phase,

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T. Hongo · K.-i. Kondo · K. G. Nakamura (✉)
Materials and Structures Laboratory, Tokyo Institute of Technology R3-10, 4259 Nagatsuta, Yokohama 226-8503, Japan
e-mail: nakamura@msl.titech.ac.jp

T. Atou
Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-8577, Japan

hydroxide and carbonate. High pressure was generated by a lever-arm type diamond anvil cell [15] with 4:1 methanol–ethanol mixture as pressure medium. Small chips of ruby and powder sample were put in a hole (200-μm diameter) of a metal gasket made of the 301 stainless steel. The culet size of the anvil was 400 μm. Pressure was measured by the shift of ruby R1 line [16]. The 532 nm line of a laser beam from a diode-pumped Nd:YAG laser (Coherent Inc., Compass 315M) was used for Raman exiting beam at energy of 80 mW. Raman scattering light was collected and focused into a 400 μm core optical fiber through camera lenses and introduced into a spectrometer (Kaiser Optical Systems, inc., Holospec f/1.8i). The dispersed light was detected with an intensified charge coupled device camera (Andor Technology Ltd., ICCD-420). The spectral resolution is about 3 cm^{-1}.

Results and discussion

Raman spectra of Sm_2O_3 in the pressure increasing process from ambient pressure up to 21.0 GPa are given in Fig. 1a. At ambient pressure, 7 lines at 247, 281, 373, 405, 418, 458, and 574 cm^{-1} were observed. The factor group analysis for the B-type structure predicts 21 Raman active modes ($14A_g + 7B_g$). According to the reported assignment of B-type Sm_2O_3 [17], the observed lines at 247, 458, and 574 cm^{-1} were assigned to A_g modes. The lines at 281 cm^{-1} and 405 cm^{-1} were assigned to B_g modes, and the lines at 373 cm^{-1} and 418 cm^{-1} were assigned to overlapping with B_g and A_g modes. The band of 247 cm^{-1} split into two bands as pressure increased to 2.0 GPa.

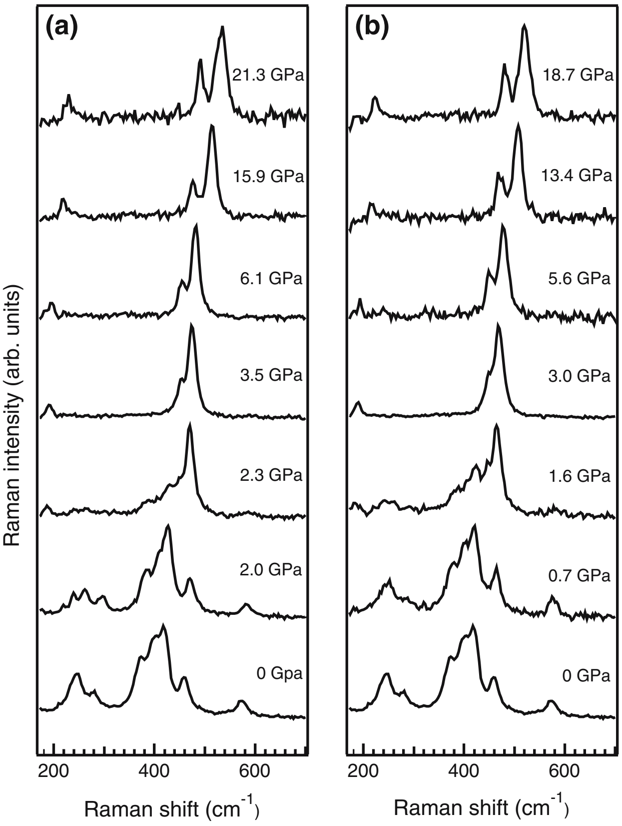

Fig. 1 Raman spectra of Sm_2O_3 recorded between ambient pressure and 21.0 GPa (**a**), 21.0 GPa and ambient pressure (**b**)

Between 2.0 GPa and 2.6 GPa, two phases coexisted, the initial monoclinic B-type phase and a new phase. Above 2.6 GPa, only the new phase was present. This new phase could be identified as the A-type hexagonal phase of Sm_2O_3 by comparing with the reported A-type Raman spectrum [17]. Also, this result is consistent with the in situ X-ray powder diffraction experiment previously reported, in which a phase transition pressure from the B-type to the A-type structure was determined to be 2.5 GPa at room temperature [13]. At 3.0 GPa, 3 lines at 188, 451, and 471 cm^{-1} were observed in this work. The A-type contains one formula unit per cell and the factor group analysis for the A-type structure predicts 4 Raman active modes ($2A_g + 2E_g$). Since the A-type Sm_2O_3 can be stabilized at ambient pressure by adding about 5 mol% ZrO_2, the A-type Raman spectrum at ambient pressure has been reported: i.e., two stretching modes at 455 cm^{-1} and 444 cm^{-1} and two bending modes at 188 cm^{-1} and 105 cm^{-1} [17]. By comparing the observed 3 lines with those of the zirconium stabilized A-type Sm_2O_3, the observed lines at 188 cm^{-1} and 451 cm^{-1} can be assigned to A_g modes and the line at 471 cm^{-1} can be assigned to E_g mode, if slight pressure variation of the observed Raman shift is taken into account. One of the bending modes reported at 105 cm^{-1} was not observed in the present experiment. The A-type Raman spectra showed no appreciable change, revealing that the A-type Sm_2O_3 was stable up to 21.0 GPa.

On the other hand, the Raman spectra of Sm_2O_3 obtained from 21.0 GPa down to ambient pressure are given in Fig. 1b. The A-type phase was stable down to 1.8 GPa, whereas the B-type phase appeared below 1.8 GPa. The A-type phase and B-type mixed phase was observed down to 1.1 GPa. Below 1.1 GPa, only B-type phase was present, and the spectra showed no appreciable change against pressure down to ambient pressure.

Figure 2 shows yield of the A-type phase as a function of pressure. The yield was determined by the intensity ratio of the B-type and the A-type phase Raman spectra. Solid curves in the figure are guide for eyes. The B-type structure begins to transform to the A-type structure above 2.0 GPa in the pressure increasing process. On the other hand, when

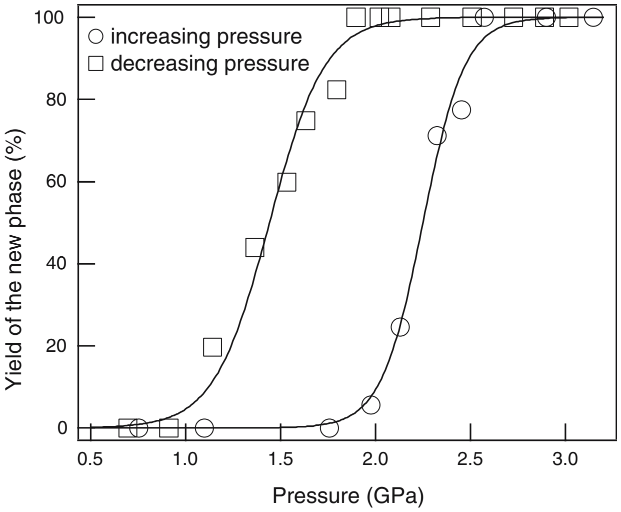

Fig. 2 The yield of the new phase as a function of pressure

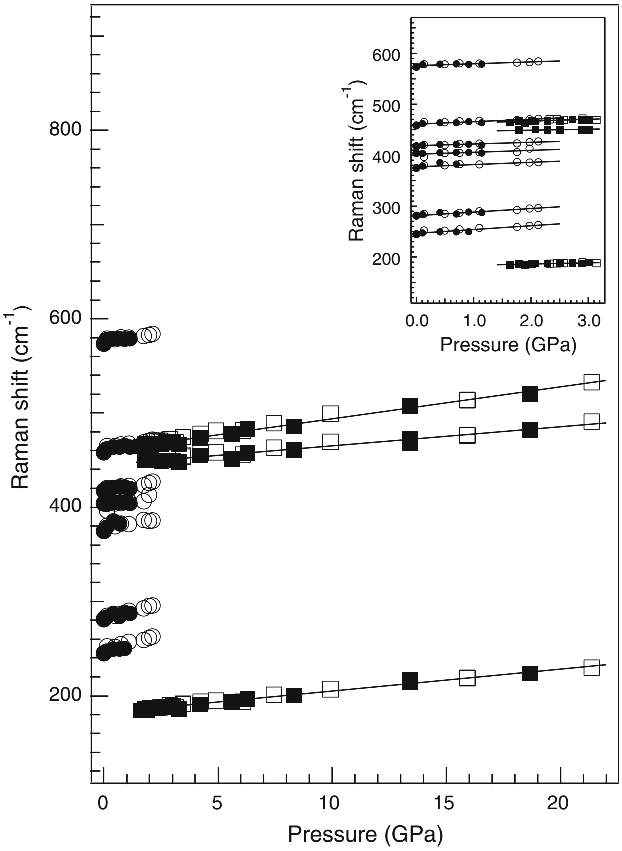

Fig. 3 Evolution of Raman frequencies of Sm_2O_3 between ambient pressure and 21.0 GPa as a function of pressure. Open and filled circles correspond to increasing and decreasing pressure runs, respectively. The inset is the magnified figure between ambient pressure and 3.2 GPa

the pressure is lowered, the A-type structure remained until 1.1 GPa. This transition is thus reversible with a hysteresis of almost 1.0 GPa.

Figure 3 shows evolutions of the frequencies as a function of pressure. Open and filled circles correspond to increasing and decreasing pressure runs, respectively. All of them show linear dependences with pressure. In the pressure both increasing and decreasing processes, they showed no appreciable hysteresis in the Raman frequency shifts of the initial B-type phase and the high pressure transformed A-type phase. The Raman lines were shifted toward the higher frequencies (2–6%). This should be related to the contraction of Sm–O bonds under high pressures [3]. The two bands at 451 cm^{-1} and 471 cm^{-1} of the A-type phase at 3.0 GPa showed different pressure dependences. The linear pressure coefficients are estimated to be 2.0 cm^{-1} and 3.4 cm^{-1}/GPa for the bands at 451 cm^{-1} and 471 cm^{-1}, respectively.

The unit cell of the B-type monoclinic structure can be expressed by six distorted units of the A-type hexagonal cell [12, 17]. Thus, this phase transition can be brought by small atomic displacements. However, no soft mode band was observed in the pressure increasing and decreasing processes, indicating that this transition was first order phase transition and the lattice vibration observed by Raman scattering did not participate in the phase transition.

The B-type to the A-type phase transition of the other rare earth sesquioxides is reported for Eu_2O_3 and Gd_2O_3. The B-type Eu_2O_3 and Gd_2O_3 transformed to the A-type phase at about 4 GPa and 7 GPa, respectively [13, 18]. The ionic radii of trivalent samarium, europium, and gadolinium cations are 0.958, 0.947, and 0.938 Å. The phase transition pressure increases as the ionic radii decrease, revealing that the transition pressure of this phase transition is mainly governed by geometric factors determined by the ionic radius ratio between cation and oxide anion.

In this work, we have shown the pressure effect on the structure change of Sm_2O_3. The reversible pressure induced phase transition from the B-type to the A-type structure was demonstrated. The B-type structure was unstable above 2.0 GPa in the pressure increasing process, and transformed to the hexagonal A-type structure. The B-type and the A-type phase coexisted between 2.0 GPa and 2.6 GPa. The A-type structure was stable up to 21.0 GPa, and Raman frequencies increased with pressure. The B-type structure appeared below 1.8 GPa, and the A-type and B-type mixed phase was observed down to 1.1 GPa in the pressure decreasing process. The phase transition exhibits a hysteresis of almost 1.0 GPa.

Acknowledgments The authors thank S. Oguchi for his assistance in experiments.

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