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High-pressure and high-temperature synthesis of heavy lanthanide sesquisulfides Ln_2S_3 (Ln=Yb and Lu)

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ABSTRACT

Detailed pressure-temperature phase diagrams of heavy lanthanide sesquisulfides Ln_2S_3 (Ln = Yb and Lu) have been investigated by in-situ x-ray diffraction experiments under high pressure and high temperature using synchrotron radiation and multi-anvil press. Based on the results of the in-situ observation, the single γ-phase (Th_3P_4-type structure, $I\bar{4}3d$) samples of Ln_2S_3 (Ln = Yb and Lu) have been synthesized under high pressure. The physical properties of the compounds were studied by electrical resistivity, specific heat, and magnetic susceptibility measurements between 2 K and 300 K.

1. Introduction

Heavy-lanthanide sesquisulfides Ln_2S_3 (Ln = Lanthanide) have seven forms of crystal structure [1]. Among them, the γ-phase (cubic, $I\bar{4}3d$), which has Th_3P_4-type structure, is expected for high-performance thermoelectric materials or optical materials [2–4]. However, the γ-phase of heavy-lanthanide sesquisulfides Ln_2S_3 are difficult to synthesize at ambient pressure. While it has been reported that Lu_2S_3 was about 50% converted from the ε phase (rhombohedral, $R\bar{3}c$) to the γ-phase under high pressure and high temperature [5], a high-quality single phase sample of γ-Lu_2S_3 has not been obtained so far. In this study, we have tried to synthesize samples of γ-Lu_2S_3 under high pressure using a low-pressure phase (named ζ-phase, orthorhombic Sc_2S_3-type structure, $Fddd$) [6] and the elements as starting materials. In order to obtain the optimum condition for preparing high-quality samples of γ-Lu_2S_3 under high pressure, detailed pressure-temperature (P-T) phase diagrams of Lu_2S_3 and a analogue compound Yb_2S_3 for comparison have been investigated by in-situ x-ray diffraction experiments using synchrotron radiation. Based on the optimum condition decided by the in-situ observation, the single γ-phase samples of Ln_2S_3 (Ln = Yb and Lu) have been synthesized. Furthermore, the fundamental physical properties have been investigated.

2. Experimental

In-situ x-ray diffraction patterns were taken by an energy dispersive method using synchrotron radiation and a solid-state detecter. High pressure was applied using a multi-anvil assembly 6-6 (MA6-6) [7] with a cubic-anvil high-pressure apparatus, the MAX80 system, installed at the beam line AR-NE5C, at Photon Factory (PF) in High Energy Accelerator Research Organization (KEK) (Tsukuba, Japan). The MA6-6 consists of six small second-stage anvils with an anvil guide, and can be compressed by a cubic-anvil apparatus. The truncated edge length (TEL) of the second-stage anvil made of tungsten carbide is 4 mm. The anvil guide is made of tool steel (SUS304), with an outer edge length of 28 mm. The anvil guide has holes along one of the diagonal direction for access to the incident and exiting x-rays. The TEL of the first-stage anvil is 27 mm. The sample container made of phyrophilite is formed into a cube of 7 mm on an edge. The starting materials, which are ζ-phase ($Fddd$) powder samples or mixture of rare earth metals and sulfur, are put into a BN crucible. The crucible with a graphite heater is inserted in a cube-shaped phyrophilite

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solid pressure medium. Pressure was determined by the lattice constant of NaCl internal pressure marker. The details of the in-situ observation method were described in previous report [8]. To measure in-situ x-ray diffraction pattern of Lu_2S_3 above 8 GPa, we used a Kawai-type double-stage multi-anvil high-pressure apparatus, the SPEED-1500 system [9], installed at the beam line BL04B1 at SPring-8, Japan. The powder samples of ζ-Yb_2S_3 and ζ-Lu_2S_3 for the starting materials were synthesized by means of CS_2 gas sulfidation method [10].

X-ray powder diffraction patterns of ζ-Lu_2S_3 (*Fddd*) at room temperature and high pressures were measured with a diamond-anvil cell (DAC) and an imaging plate using synchrotron radiation. High-pressure diffraction experiments were performed at the beam line 18C at PF in KEK. We employed the DAC with diamond culet diameters of 500 μm. The sample was finely ground and loaded in the 180 μm diameter hole drilled in a stainless steel (T301) gasket. The pressure in the DAC was measured before and after each exposure based on the shifts of the ruby R1 and R2 fluorescence lines. A 4:1 methanol-ethanol solution was used as the pressure medium.

Large bulk samples of γ-Yb_2S_3 and γ-Lu_2S_3 ($I\bar{4}3d$) were prepared at high temperatures and high pressures using a Kawai-type multi-anvil high-pressure apparatus. The sample cell assembly is similar to that used for the high-pressure synthesis of filled skutterudite compounds [11,12]. The compounds were prepared by transition from ζ-phases (*Fddd*) or reacting stoichiometric amounts of 3N (99.9% pure)-Yb, Lu chips, and 6N-S powder at 3–8 GPa. The reaction temperatures were between 1200 and 1800 °C. The prepared samples were characterized by powder x-ray diffraction using Co $K\alpha_1$ radiation and silicon as a standard. The chemical compositions were verified by scanning electron microscope (SEM) with energy dispersive x-ray spectrometer (EDX, JEOL). Resistivity was measured by a standard dc four-probe method. Magnetization was measured with a Quantum Design MPMS superconducting quantum interference device magnetometer. The specific heat was measured by a thermal relaxation method (PPMS; Quantum Design).

3. Results and discussion

3.1. Sample preparation and P-T phase diagram of Yb_2S_3

Fig. 1 shows some of the in-situ x-ray diffraction patterns of Yb_2S_3 using ζ-Yb_2S_3 (*Fddd*) powder as starting materials. Fig. 1(a) shows x-ray diffraction pattern of the starting material ζ-Yb_2S_3 (*Fddd*) at room temperature and 3 GPa. Solid squares indicate the characteristic x-ray for Yb. Open circles indicate the Bragg peaks of ζ-Yb_2S_3 (*Fddd*). On increasing the pressure, no changes in the diffraction patterns could be observed except shifting of peaks due to lattice compression. This trend is observed until 5.5 GPa. Absence of any additional diffraction peak with pressure indicates that the material is structurally stable under compression up to 5.5 GPa at least. With increasing temperature, the Bragg peaks of ζ-Yb_2S_3 (*Fddd*) faded out, and then the peaks of $YbS_{1.7}$ (tetragonal NdS_2-type structure [13], $P\bar{4}b2$) were observed above 400 °C (Fig. 1(b)). At the same time, Yb oxysulfide Yb_2O_2S (monoclinic, $P2_1/c$) [14] as an impurity phase was detected. Above 1100 °C $YbS_{1.7}$ ($P\bar{4}b2$) started to change to III-Yb_2S_3 (orthorhombic U_2S_3-type structure [1], *Pnma*)

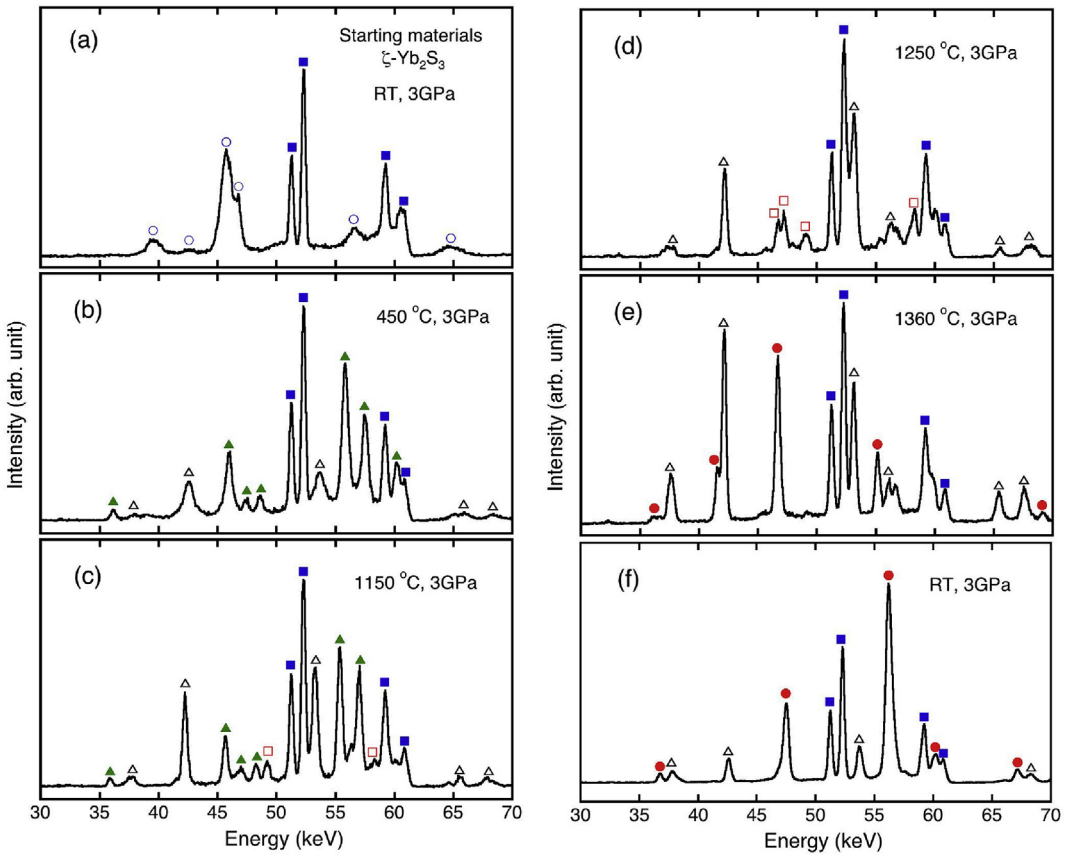

Fig. 1. X-ray diffraction patterns of heating process of ζ-Yb_2S_3 (*Fddd*) at 3 GPa. Open circles designate the Bragg peaks of ζ-Yb_2S_3 (*Fddd*). Solid squares indicate the characteristic x-ray for Yb. Solid triangles, open squares and solid circles designate the Bragg peaks of $YbS_{1.7}$ ($P\bar{4}b2$), III-Yb_2S_3 (*Pnma*) and γ-Yb_2S_3 ($I\bar{4}3d$), respectively. Open triangles indicate the peaks of Yb_2O_2S ($P2_1/c$). (a) The starting materials (ζ-Yb_2S_3) at room temperature, (b) 450 °C, (c) 1150 °C, (d) 1250 °C, (e) 1360 °C and (f) room temperature after quenching.