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Structural phase transition of ScSb and YSb with a NaCl-type structure at high pressures

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Abstract

By use of synchrotron radiation, powder X-ray diffraction of ScSb and YSb with a NaCl-type structure has been studied up to 45 GPa at room temperature. A first-order phase transition from the NaCl-type (B1) to a CsCl-type structure (B2) began to occur at around 28 GPa for ScSb and at around 26 GPa for YSb. Crystal data of the high-pressure phase of both antimonides are obtained. The high-pressure structural behavior of ScSb and YSb is similar to that of heavier LnSb (Ln = Dy–Lu). The B1–B2 transition for ScSb and YSb can be understood according to the rigid sphere model. The bulk moduli of ScSb and YSb are about 58 GPa at ambient pressure.

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Keywords: B. Chemical synthesis; C. Crystal structure and symmetry; D. Phase transitions; E. Strain, high pressure; E. Synchrotron radiation

1. Introduction

The high-pressure structural behavior of binary AB compounds with a NaCl-type structure has been a popular topic in condensed matter research. The majority of these compounds undergo the first-order structural phase transition from the NaCl-type (B1) to the CsCl-type (B2) structure at high pressures. Lanthanide monoantimonides LnSb (Ln = lanthanide) have the NaCl-type structure at ambient pressure. By use of synchrotron radiation, powder X-ray diffraction of LnSb with the NaCl-type structure has systematically been studied up to 45 GPa at room temperature. First-order phase transitions with the crystallographic change occur for LnSb at high pressures [1–4]. The structure of high-pressure phases of LnSb is classified into three groups [3]. The lighter LnSb (Ln = La, Ce, Pr and Nd) have a tetragonal structure (distorted CsCl-type) at high pressures. The high-pressure form of the middle LnSb (Ln = Sm, Gd and Tb) is unknown. The heavier LnSb (Ln = Dy, Ho, Er, Tm and Lu) show the B1–B2 transition at high pressures though the same transition is not observed in the heavier LnP and LnAs [5,6]. The transition pressures of LnSb do not depend on the structure of their high-pressure phases, but increase with decreasing lattice constant in the NaCl-type structure [3]. A lattice constant of YSb with the NaCl-type structure almost agrees with that of DySb. It is expected that the pressure-induced phase transition of YSb is similar to that of heavier LnSb. The lattice constant of ScSb with the NaCl-type structure is much smaller than that of LuSb. Thus, the high-pressure structural behavior in ScSb is very interest.

By use of synchrotron radiation, we have studied powder X-ray diffraction of ScSb and YSb with the NaCl-type structure up to 45 GPa at room temperature and found the B1–B2 transition at high pressures. In this paper the high-pressure structural behavior of ScSb and YSb is discussed.

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2. Experimental

ScSb and YSb were prepared by reaction of stoichiometric amounts of each rare earth metal and antimony in a sealed silica tube at around 800 °C. These compounds prepared by us were characterized by powder X-ray diffraction using Cu Kα radiation and silicon as a standard. By use of synchrotron radiation, powder X-ray diffraction patterns of ScSb and YSb were measured with a diamond-anvil cell and an imaging plate up to 45 GPa at room temperature [2–4]. Incident beam was monochromatized by Si (111) crystals. The pressure in the diamond-cell was determined from a pressure shift In the sharp R-line fluorescence spectrum of ruby. A 4:1 methanol–ethanol solution was used as the pressure-transmitting fluid.

3. Results and discussion

Fig. 1 shows powder X-ray diffraction patterns of ScSb at high pressures. The profile indicates only characteristic lines of the NaCl-type structure at around 1.5 GPa. The *d*-values of 111, 200, 220, 311, 222, 400, 331, 420, 422, 511, 440, 531, 600, 620 and 622 lines of ScSb decrease with increasing pressure up to 25 GPa. New diffraction lines appear at around 28 GPa and grow with increasing pressure. The characteristic lines of the CsCl-type structure are observed in the new high-pressure phase. A single phase of the high-pressure form is obtained above 43 GPa. X-ray diffraction data of this single phase of ScSb are given in Table 1. All lines of the high-pressure phase are indexed in the cubic CsCl-type structure. Crystal data of the single phase of ScSb are $a = 3.36(1)$ Å, $V = 37.9(5)$ Å^3 at 43 GPa.

Table 1
X-ray diffraction data of the high-pressure form (single phase) of ScSb

ScSb at 43 GPa						
h	*k*	*l*	*d* (obs.)	*d* (cal.)	I/I_0 (obs.)	I/I_0 (cal.)
1	0	0	3.576	3.357	40	25
1	1	0	2.361	2.374	100	100
1	1	1	1.950	1.938	22	8
2	0	0	1.704	1.679	8	19
2	1	0	1.474	1.501	5	13
2	1	1	1.377	1.371	14	40
2	2	0	1.186	1.187	20	13

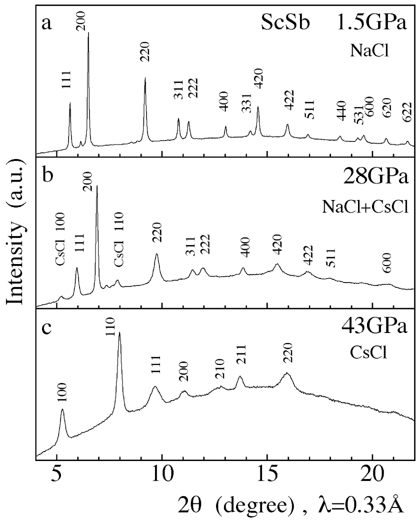

Fig. 1. Powder X-ray diffraction patterns of ScSb at high pressures: (a) NaCl-type structure; (b) Coexistence of NaCl- and CsCl-type structures; (c) CsCl-type structure.

Fig. 2 shows the cell volume/formula unit vs pressure curve for ScSb. The cell volume with the NaCl-type structure monotonically decreases with increasing pressure up to 28 GPa. The structural change to the CsCl-type structure occurs with the volume collapse of about 1% at around 34 GPa. When the pressure is removed, the diffraction lines of the NaCl-type structure reappear at around 10 GPa. The experimental data can be fitted by a Birch equation of state [7]:

$$P = (3/2)B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 - 3/4(4 - B_0') \times [(V/V_0)^{-2/3} - 1]\} \qquad (1)$$

where B_0 is the bulk modulus, B_0' its first pressure derivative, V the volume, and P is the pressure. A least-squares fit to the data of ScSb gives the following values: $B_0 = 58 \pm 3$ GPa and $B_0' = 9.5 \pm 0.8$.

Fig. 3 shows the Sc–Sc and Sc–Sb distances in ScSb at high pressures. The Sc–Sb distance in the NaCl-type structure is 2.92 Å at ambient pressure. This distance is much shorter than the sum of ionic radii of Sc^{3+} (0.81 Å) and Sb^{3-} (2.45 Å). The Sc–Sb distance is slightly shorter than the sum of the atomic radius of Sc (1.62 Å) and the covalent radius of Sb (1.38 Å), longer than the sum of the covalent radii of Sc (1.44 Å) and Sb (1.38 Å). Thus, the chemical bond between Sc and Sb atoms has the covalent

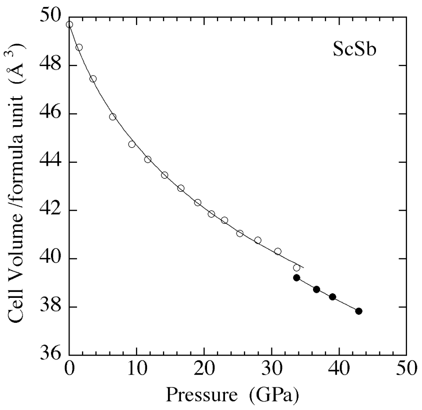

Fig. 2. Cell volume/formula unit vs pressure curve for ScSb.

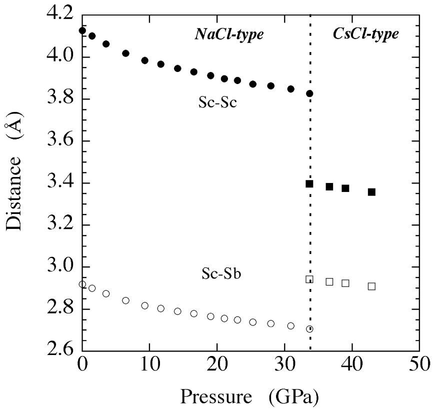

Fig. 3. Sc–Sc and Sc–Sb distances in ScSb at high pressures.

character. When the B1–B2 transition occurs at around 34 GPa, the Sc–Sb distance suddenly increases and becomes 2.94 Å in the CsCl-type structure. This almost agrees with the Sc–Sb distance (2.92 Å) in the NaCl-type structure at ambient pressure. On the other hand, the Sc–Sc distance in ScSb abruptly decreases if the B1–B2 transition occurs.

Fig. 4 shows powder X-ray diffraction patterns of YSb at high pressures. Characteristic lines of the NaCl-type structure shift to the high degree region with increasing pressure. New diffraction lines appear at around 26 GPa and grow with increasing pressure. Low- and high-pressure phases coexist between 26 and 36 GPa. The single phase of the high-pressure form is obtained above 37 GPa. X-ray diffraction data of this single phase of YSb are given in Table 2. All lines are indexed in the cubic CsCl-type structure. Crystal data of the single phase of YSb are $a = 3.53(1)$ Å, $V = 44.0(5)$ Å^3 at 37 GPa. The cell volume vs pressure curve for YSb can be fitted by a Birch equation of state. A least-squares fit to the data of YSb gives the following values: $B_0 = 58 \pm 3$ GPa and $B_0' = 6.2 \pm 0.6$.

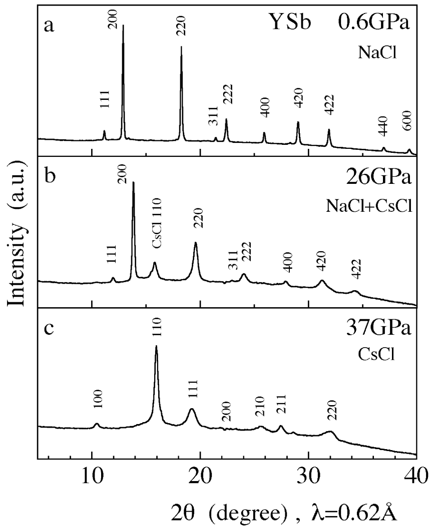

Fig. 4. Powder X-ray diffraction patterns of YSb at high pressures: (a) NaCl-type structure; (b) coexistence of NaCl- and CsCl-type structures; (c) CsCl-type structure.

Table 2
X-ray diffraction data of the high-pressure form (single phase) of YSb

Ysb at 37 GPa

h	k	l	d (obs.)	d (cal.)	I/I_0 (obs.)	I/I_0 (cal.)
1	0	0	3.777	3.532	6	3
1	1	0	2.483	2.498	100	100
1	1	1	2.062	2.039	22	1
2	1	0	1.560	1.580	6	1
2	1	1	1.452	1.442	9	43
2	2	0	1.248	1.249	8	14

Crystal data of the high-pressure form for ScSb, YSb and heavier LnSb (Ln = Dy, Ho, Er, Tm and Lu) are summarized in Table 3. These compounds show the B1–B2 transition at high pressures. It is well known that ionic crystals like the alkali halide have the CsCl-type structure if the ratio of their ionic radii (r_c/r_a) is above 0.732. As mentioned above, ScSb is not the simple ionic crystal. The Sc–Sb distances in the CsCl-type structure almost agree with the sum of the atomic radius (R_{Sc}) of Sc and the covalent radius (R_{Sb}) of Sb. The ratio of their radii ($R_{Sb}/R_{Sc,Y}$) is 0.85 for ScSb and 0.77 for YSb. These values suggest that ScSb and YSb have the 8 coordination (CsCl-type structure) at high pressures. Thus, the structure of high-pressure form of both compounds can be understood according to the rigid sphere model. The high-pressure structural behavior of ScSb and YSb is similar to that of heavier LnSb, but does not resemble that of LaSb that changes from the B1 to the tetragonal structure at high pressure. This must arise from the large atomic radius of La (1.87 Å).

Fig. 5 shows transition pressures vs lattice constants in the NaCl-type structure for metal monoantimonides, MSb (M = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu). X-ray diffraction of LaSb and CeSb has already been studied at high pressures [1]. We have again

Table 3
Crystal data of the high-pressure form (single phase) for the heavier LnSb (Ln = Dy, Ho, Er, Tm, Lu), YSb and ScSb

Compound	P (GPa)	Structure	a (Å)	V (Å^3)
ScSb	43	CsCl-type	3.36(1)	37.8(5)
YSb	37	CsCl-type	3.53(1)	44.0(5)
DySb	28	CsCl-type	3.54(1)	44.5(5)
HoSb	31	CsCl-type	3.57(2)	45.5(6)
ErSb	35	CsCl-type	3.50(3)	43.0(9)
TmSb	31	CsCl-type	3.46(1)	41.6(5)
LuSb	33	CsCl-type	3.46(2)	41.5(6)

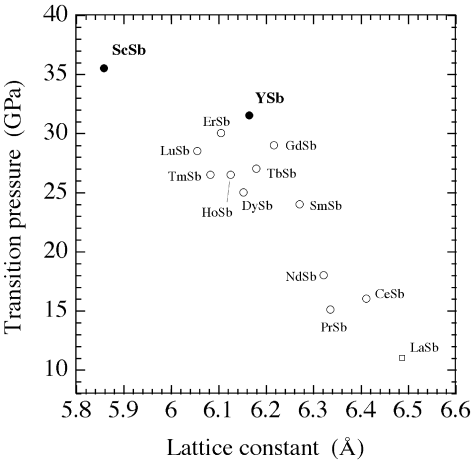

Fig. 5. Transition pressures vs lattice constants curve in the NaCl-type structure for metal monoantimonides, MSb (M = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu); the transition pressure of LaSb has been studied by Leger et al. [1]. Black circle shows the present work.

investigated the pressure-induced phase transition of CeSb with synchrotron radiation [8]. The transition pressure of CeSb is 4 GPa higher than the results obtained by Leger et al. The transition pressures of these compounds increase with decreasing lattice constant in the NaCl-type structure. The structure of the high-pressure phase of MSb is classified into three groups. The lighter LnSb (Ln = La, Ce, Pr and Nd) have the tetragonal structure (distorted CsCl-type). The high-pressure form of the middle LnSb (Ln = Sm, Gd and Tb) is unknown. On the other hand, the heavier LnSb (Ln = Dy, Ho, Er, Tm, and Lu), YSb and ScSb show the typical B1–B2 transition at high pressures. As mentioned above, the structure of high-pressure form of these antimonides can be understood according to the rigid sphere model. The high-pressure structural behavior in the heavier LnSb (Ln = Dy, Ho, Er and Tm) with many f electrons is similar to that of LuSb, YSb and ScSb. Thus, the pressure-induced phase transition in the heavier LnSb is insensitive to the f electrons.

Fig. 6 shows the electrical resistivity of ScSb with the NaCl-type structure at low temperatures. The resistivity of the compound decreases linearly to temperature from 280 down to 75 K. ScSb shows the metallic behavior below room temperature. This result suggests that ScSb does not behave as a simple ionic compound $Sc^{3+}Sb^{3-}$.

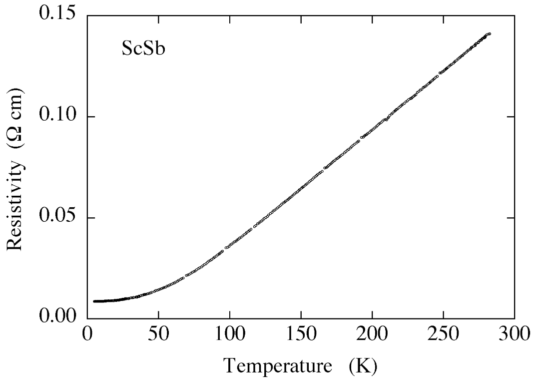

Fig. 6. Electrical resistivity of ScSb with the NaCl-type structure at low temperatures.

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