Pressure-induced phase transition of SmBi with a NaCl-type structure

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Abstract. By use of synchrotron radiation, powder x-ray diffraction of SmBi with a NaCl-type structure has been studied up to 30 GPa at room temperature. A first-order phase transition began to occur at around 16.2 GPa. SmBi transformed from the NaCl-type (B1) to the tetragonal (distorted CsCl-type) structure with the volume collapse of about 8.2 % at around 18.3 GPa. Crystal data of the single phase are \( a = 3.775(5) \) Å, \( c = 3.25(2) \) Å, \( c/a = 0.86 \) and \( V = 46.4(3) \) Å\(^3\) at 20.3 GPa. The high-pressure form of SmBi is isostructural with that of SmAs. A bulk modulus of SmBi was estimated from the volume vs. pressure curve fitted by a Birch equation of state. The bulk modulus (\( B_0 \)) and its pressure derivative (\( B'_0 \)) are 68 ± 3 GPa and 3.9 ± 0.3, respectively. The transition pressure and the bulk modulus of SmBi are larger than those of CeBi and PrBi. The structural high-pressure behaviour for SmX (\( X = P, As, Sb \) and Bi) is discussed. The structural phase transition of LaBi and NdBi occurred at around 11.5 GPa and 16.8 GPa, respectively. The transition pressures of LnBi (\( Ln = La, Ce, Pr, Nd \) and Sm) decreased with increasing lattice constant.

1. Introduction
By use of synchrotron radiation, powder x-ray diffraction of various lanthanide monopnictides, \( LnX \) (\( Ln = \) lanthanide; \( X = P, As \) and Sb) with a NaCl-type structure has systematically been studied up to 60 GPa at room temperature [1]. Pressure-induced phase transitions of \( LnP \) have been found at room temperature. The lighter \( LnP \) (\( Ln = La, Ce, Pr \) and Nd) transform from the NaCl-type (B1) to the CsCl-type (B2) or the tetragonal (distorted CsCl-type) structure at high pressures [2, 3]. First-order phase transitions of \( LnAs \) with the crystallographic change occur at high pressures [4, 5]. The structure of the high-pressure phases of \( LnSb \) is classified into three groups [6-8]. The lighter \( LnSb \) (\( Ln = La, Ce, Pr \) and Nd) have the tetragonal structure 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. The electronic and structural properties of some lanthanide pnictides at high pressure have theoretically been studied by several investigators [9-11].

Structural phase transitions of SmX (\( X = P, As \) and Sb) with the NaCl-type structure have already been investigated at high pressures. SmAs transforms from the B1 to the tetragonal structure at around 32.1 GPa [4]. In contrast, the high-pressure form of SmP and SmSb is unknown [2, 5]. The structural phase transitions of CeBi and PrBi occur at around 13 GPa and 14 GPa, respectively [3, 12]. The
crystal structure of both bismuthides changes from the B1 to the B2 and tetragonal structures at high pressures. Both structures in the high–pressure phase coexist in a wide pressure range. Vaitheeswaran et al. have performed the theoretical study for the lattice instability of LaBi at high pressures, and have predicted that LaBi shows the phase transition at around 11.2 GPa [13].

Using synchrotron radiation, we have investigated powder x-ray diffraction of SmBi with the NaCl-type structure up to 30 GPa at room temperature, and found the first-order phase transition at around 16.2 GPa. The structure of the high-pressure phase of SmBi is determined. The structural high-pressure behavior of SmX (X = P, As, Sb and Bi) is discussed.

2. Experimental

SmBi with the NaCl-type structure was prepared by reaction of stoichiometric amounts of Sm and Bi elements in a sealed silica tube at around 700 °C for 72 hours. This bismuthide was characterized by powder x-ray diffraction using CuKα radiation and silicon as a standard. The lattice constant of SmBi is \( a = 6.364 (1) \) Å at ambient pressure. This value almost agrees with the result of Iandelli [14].

Using synchrotron radiation, powder x-ray diffraction patterns of SmBi were measured with a diamond-anvil cell (DAC) and an imaging plate up to 30 GPa at room temperature [6-8]. We employed the DAC with diamond culet diameters of 500 μm. The sample was finely ground and loaded in the 100 μm diameter hole drilled in a stainless steel (T301) gasket. The synchrotron radiation experiments (proposal number: 2005A0723) were performed at the BL04B2 in the SPring-8. The incident beam was monochromatized by a Si (1 1 1) double crystal to a wavelength of 0.3280 Å. The pressure in the diamond-cell was measured before and after each exposure based on the shifts of the ruby R1 and R2 fluorescence lines. Fluorinert mixture was used as pressure medium.

3. Results and discussion

Figure 1 shows powder x-ray diffraction patterns of SmBi at high pressures. The profile indicates only characteristic lines of the NaCl-type structure at normal pressure. The \( d \)-values of 111, 200, 220, 222, 400, 420, 422, 440, 600, 620 and 622 lines monotonically decrease with increasing pressure up to 16 GPa. New diffraction lines begin to appear at around 16.2 GPa and grow with increasing pressure. The 110 line of the CsCl-type structure expected as the high-pressure form is split into two lines 110 and

![Figure 1. Powder x-ray diffraction patterns of SmBi at high pressures.](image-url)
101 in the tetragonal structure. X-ray diffraction data of the high-pressure form of SmBi are given in table 1. All diffraction lines of this phase are indexed in the tetragonal structure. Crystal data of the single phase at 20.3 GPa are \(a = 3.775(5) \, \text{Å}, \ c = 3.25 \, \text{(2) Å}, \ c/a = 0.86 \) and \(V = 46.4(3) \, \text{Å}^3\). We have already found the structural phase transition of SmAs at high pressure; this arsenide transforms from the B1 to the tetragonal structure at around 32.1 GPa [4]. The high-pressure form of SmBi is isostructural with that of SmAs. As mentioned above, the phase transitions with the structural change take place at around 13 GPa for CeBi [12] and 14 GPa for PrBi [3]. The tetragonal and B2 structures in the high-pressure phase coexist in a wide pressure range. In contrast, there is only the tetragonal structure in the high-pressure phase of SmBi.

Figure 2 shows a cell volume/formula unit vs. pressure curve for SmBi. The cell volume monotonically decreases with increasing pressure up to 16 GPa. The structural change to the tetragonal structure occurs with the volume collapse of about 8.2 % at around 18.3 GPa. When the pressure is removed, the diffraction lines of the NaCl-type structure reappear at around 8 GPa. The cell volume vs. pressure curve can be fitted by a Birch equation of state [15]:

\[
P = \frac{3}{2} B_0 \left( \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right) \left\{ 1 - \frac{3}{4} \left( \frac{V}{V_0} \right)^{2/3} - 1 \right\} \]

where \(B_0\) is the bulk modulus, \(B_0'\) its first pressure derivative, \(V\) the volume and \(P\) the pressure; the subscript zero refers to values at normal pressure. A least-square fit to the data of SmBi give the following values: \(B_0 = 68 \pm 3 \, \text{GPa}, B_0' = 3.9 \pm 0.3\). The bulk modulus of CeBi and PrBi is 49.6 and 40 GPa, respectively [3, 12]. These values are smaller than the bulk modulus of SmBi.

The lattice constant and the bulk modulus with the NaCl-type structure, the transition pressure and the structure of the high-pressure phase for Sm\(X\) (\(X = \text{P, As, Sb and Bi}\)) are summarized in table 2. The transition pressure of Sm\(X\) decreases with increasing lattice constant. We have already

| Table 1. X-ray diffraction data of the high-pressure form of SmBi at 20.3 GPa. |
|---------------------|--------|--------|--------|--------|
| \(h\) | \(k\) | \(l\) | \(d\) (obs.) | \(d\) (cal.) | \(I/I_0\) (obs.) | \(I/I_0\) (cal.) |
| 1 | 1 | 0 | 2.6638 | 2.6701 | 100 | 61 |
| 1 | 0 | 1 | 2.4623 | 2.4675 | 81 | 100 |
| 2 | 0 | 0 | 1.8962 | 1.8881 | 35 | 25 |
| 2 | 1 | 1 | 1.4992 | 1.4995 | 45 | 53 |
| 2 | 2 | 0 | 1.3331 | 1.3351 | 28 | 21 |
investigated powder x-ray diffraction of PrX (X = P, As, Sb and Bi) at high pressure. The transition pressures of PrX are 26 GPa for PrP, 27.1 GPa for PrAs, 13 GPa for PrSb and 14 GPa for PrBi [3]. The transition pressure of PrP is slightly lower than that of PrAs. PrSb has lower transition pressure compared with PrBi. Figure 3 shows transition pressure vs. lattice constant curves for the SmX and PrX (X = P, As, Sb and Bi). The transition pressures of LnP (Ln = Pr and Sm) are close to those of LnAs. LnSb and LnBi (Ln = Pr and Sm) have near transition pressure. In the previous paper, we have suggested that the transition pressures of LnX (Ln = La, Ce and Pr; X = P, As, Sb and Bi) are classified into two groups, P and As compounds and Sb and Bi compounds [16]. The similar tendency is also found for SmX. The transition pressure of SmSb is about 13 GPa lower than that of SmAs. The lattice constant of Sm pnictides abruptly increases between SmAs and SmSb as shown in table 2. This increase lowers markedly the transition pressure of SmSb. The high-pressure forms of SmP and SmSb are unknown. In contrast, SmBi and SmAs have the tetragonal structure above the transition pressures. The structural behavior of SmSb and SmBi is very different at high pressure though the transition pressure of SmBi is close to that of SmSb. Thus, the structural high-pressure behavior of SmX (X = P, As, Sb and Bi) is very interesting.

The bulk modulus of SmAs is larger than those of SmP. The similar behavior is also observed for PrP and PrAs [3]. Generally, the bulk modulus vs. cell volume curves plotted on a log-log scale show the linear relationship for various AB compounds with the NaCl-type structure [17]. However, the bulk modulus of SmAs with the large cell volume is larger than that of SmP with the small volume. A Sm-P distance in the NaCl-type structure is 2.88 Å at ambient pressure. This distance is slightly longer than the sum of the atomic radius of Sm (1.80 Å) and the covalent radius of P (1.06 Å). On the other hand, the Sm-As distance (2.961 Å) is shorter than the sum of the atomic radius of Sm and the

| SmP  | 5.760 | 74 | 35 | unknown |
| SmAs | 5.921 | 84 | 32.1 | tetragonal |
| SmSb | 6.271 | 62 | 19 | unknown |
| SmBi | 6.364 | 68 | 16.2 | tetragonal |
covalent radius of As (1.19 Å). These results suggest that SmAs has the stronger covalent bond compared with SmP. Thus, the large bulk modulus of SmAs may arise from the increase of the covalency. The similar tendency is also observed for SmSb and SmBi.

Figure 4 shows the interatomic Sm-Sm and Sm-Bi distances in SmBi at high pressures. The Sm-Bi distance in the NaCl-type structure is 3.182 Å at normal pressure. This distance is shorter than the sum of the atomic radius of Sm (1.80 Å) and the covalent radius of Bi (1.46 Å). Thus, the chemical bond between Sm and Bi atoms has the covalent character. The Sm-Bi distance in the tetragonal structure suddenly increases at around the transition pressure. On the other hand, the Sm-Sm distance suddenly decreases when the structure changes from the B1 to the tetragonal form at around the transition pressure. The long Sm-Sm distance (3.775 Å at 20.3 GPa) along the a-axis in the tetragonal structure is longer than the sum of the atomic radius of Sm (1.80 Å). On the contrary, the short Sm-Sm distance (3.25 Å at 20.3 GPa) along the c-axis is much shorter than the sum of the atomic radius of Sm. Thus, it is expected that f-electrons in SmBi are easily delocalized along the c-axis in the tetragonal structure. The electrical and magnetic properties of SmBi have not studied at high pressure till now.

Recently, we have investigated powder x-ray diffraction of LaBi and NdBi at high pressures and found pressure-induced phase transitions with the structural change. The transitions of LaBi and NdBi occur at around 11.5 GPa and 16.8 GPa, respectively. The detail results of the high-pressure form for both bismuthides will be published elsewhere. Figure 5 shows the transition pressure vs. the lattice constant relationship for LnBi (Ln = La, Ce, Pr, Nd and Sm).
constant curve for \(LnBi\) (\(Ln = \text{La, Ce, Pr, Nd and Sm}\)). The transition pressures of the lanthanide bismuthides decrease with increasing lattice constant. In the previous papers we have investigated the relationship between the transition pressure and the atomic number of the lanthanide atoms for \(LnX\) (\(Ln = \text{lanthanide}; X = \text{P, As and Sb}\)) with the NaCl-type structure [1-8]. The transition pressure decreases with increasing lattice constant in the NaCl-type structure, which decreases with decreasing atomic number of the lanthanide atoms. As mentioned above, CeBi and PrBi undergo the structural transition from the B1 to the B2 and the tetragonal structures at high pressures [3, 12]. Both structures coexist in a wide pressure range. The similar structural behavior is not found for \(LnP\), \(LnAs\) and \(LnSb\) at high pressures. Thus, the transition pressure of \(LnX\) (\(Ln = \text{lanthanide}; X = \text{P, As, Sb and Bi}\)) does not depend on the structure of the high-pressure phase, but mainly the magnitude of the lattice constant in the NaCl-type structure.

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