Electronic phase diagram of the titanium oxypnictide superconductor BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O

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Abstract. The titanium oxypnictide superconductor is studied by resistivity, magnetization and heat capacity measurements down to 0.5 K on the powder samples of all proportional solid solution BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O. An unusual electronic phase diagram as a function of $x$ is obtained, in which a double superconducting dome with peaks at $T_c$ = 3.6 and ~4 K appears across an intervening range with lower $T_cs$ of ~1 K at 0.35 ≤ $x$ ≤ 0.55. Moreover, a sudden jump in $T_c$ is observed at $x_c$ between 0.55 and 0.60. These facts suggest unconventional mechanisms of the superconductivity of the titanium oxypnictides.

1. Introduction
Superconductivity is often observed in the proximity of other types of ordered states such as antiferromagnetic orders [1,2] and charge-density-wave (CDW) states [3]. When an ordered state is suppressed as a function of a control parameter such as carrier density or pressure, superconductivity can emerge or be enhanced with its $T_c$ increasing toward a maximum at around the vanishing point of the order. Then, the $T_c$ decreases with further increasing the control parameter. As a result, a superconducting phase with a “$T_c$ dome” occurs next to the ordered phase in the electronic phase diagram. In order to understand the mechanism of the superconductivity, it would be crucial to characterize the nature of the parent ordered phase and to elucidate its relevance to the superconducting phase. The superconducting phase is either competing with the ordered phase or is helped via fluctuations associated with the suppression of the relevant order.

The $T_c$ dome is not always a smooth single peak but can split into two peaks. In the copper oxide superconductor La$_{2-x}$Ba$_x$CuO$_4$, a dip in the $T_c$ dome is observed at $x$ ~ 0.125, which may be due to the suppression of superconductivity by a charge-ordered phase [4]. In the iron oxypnictide superconductor LaFeAs(O$_{1-x}$H$_x$), on the other hand, a distinct double dome appears as a function of electron doping by substituting H$^+$ for O$^-$ ions [5]. The two peaks have been ascribed to either of different types of structural and magnetic orders existing at around $x$ = 0 and 0.5 [6]. These observations reveal the presence of competing order parameters or reflect complex electronic structures arising from the multibands and may carry important information on the pairing mechanism.

The titanium oxypnictide with the general formula of BaTi$_2$Pn$_2$O (Pn = As, Sb, Bi) include unique superconductors found in 2012 [7-9]. They crystallize in a layered structure comprising the Ti$_2$Pn$_2$O layers separated by the Ba layers, as schematically depicted in Fig. 1. It is well established that the electronic properties are mostly governed by the Ti 3$d$ states spreading in the Ti$_2$O sheet [10]. Among the three members, the Sb and Bi compounds exhibit superconductivity at $T_c$ = 1.2 and 4.6 K,
respectively, while the As compound remains normal down to 0.5 K. On the other hand, CDW-like phases are observed at $T_{CDW} = 200$ and 50 K for the As and Sb compounds, respectively. According to the previous studies on the solid solution samples, the CDW order is gradually suppressed with increasing the Sb content starting from the As compound and disappears by a small substitution of Bi for Sb [11]. The nature of the order may not be a simple CDW type, because an accompanying superstructure has not been observed. Instead, a nematic charge order or an orbital order has been proposed [12,13]. An interesting finding in the previous study on the all proportional solid solution of BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O is the presence of two peaks in the $x$ dependence of $T_c$ [11]: as $x$ increases, the $T_c$ increases from 1.2 K at $x = 0$ to 3.5 K at $x = 0.2$, rapidly decreases below 1.85 K (the lowest measured temperature) at 0.3 < $x$ < 0.60, and suddenly rises to 4.0 K at $x = 0.60$, followed by a gradual increase to 4.6 K at $x = 1$. The first peak at small $x$ values may be related to the suppression of the CDW order, while no such nearby order has been observed for the second peak. The origin of the two $T_c$ peaks has remained mystery.

In order to clarify the complex doping dependence of $T_c$, we have carried out a systematic study on the BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O solid solution. Problems in the previous study are the limited number of samples with varying compositions and the limited measurement temperature range above 1.85 K. In addition, the difficulty in preparing samples and the easy degradation of the compounds in air have prevented one from obtaining reliable data thus far. We have carefully prepared a series of polycrystalline samples and extended the temperature range for measurements down to 0.5 K. As the result, it is revealed that the two $T_c$ peaks are not separated from each other but connected by an intervening range with low $T_C$s around 1.0 K. Moreover, the $T_c$ jumps up at $x_c$ between 0.55 and 0.60. It is suggested that a sudden change in the electronic structure and the superconductivity takes place at $x_c$.

![Figure 1](image_url)

**Figure 1.** (a) Powder x-ray diffraction profiles and (b) the composition dependence of the unit-cell volume $V$ for the solid solution BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O. The crystal structure of the titanium oxypnictides BaTi$_2$Pn$_2$O (Pn = As, Sb, Bi) is depicted in the inset of (b).

2. Experimental
A series of polycrystalline samples of BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O ($x = 0$, 0.10, 0.20, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.70, 0.80, 1) were synthesized by the conventional solid-state reaction method. A stoichiometric amount of BaO (99.99%, Aldrich), Ti (99.9%, Rare Metallic), Sb (99.99%, Rare Metallic), Bi (99.999%, Kojundo Chemical) was weighed, mixed, and pelleted in an Ar-filled glove.
box. The pellet was wrapped with a Ta foil, sealed in a quartz tube, and heated at 1000 °C for 50 hours. Then, it was slowly cooled to 300 °C at a rate of −3 °C/h before furnace-cooling to room temperature. The obtained samples were highly sensitive to air and moisture, more sensitive with increasing x. A special care was taken to minimize the degradation of the samples, as will be reported elsewhere. X-ray diffraction (XRD) experiments were performed at room temperature in a SmartLab (Rigaku) with Cu-Kα radiation. The temperature dependence of electrical resistivity was measured by a standard four-probe method in a Physical Properties Measurement System (PPMS, Quantum Design). Heat capacity was measured in the temperature range from 0.5 to 10 K by the relaxation method in a PPMS equipped with a ³He refrigerator. In order to avoid the sample degradation, a pellet was wrapped by a 0.03 mm-thick Au foil in an Ar-filled glove box, and the contribution of the Au foil was subtracted from the data. Magnetic susceptibility was measured in the temperature range from 1.8 to 7 K under 5 Oe in a SQUID magnetometer (MPMS, Quantum Design) using samples wrapped by a Parafilm (Bemis).

3. Results and discussion
All the XRD patterns of the obtained samples are nearly monophase, as shown in Fig. 1(a), and the lattice parameters vary almost linearly as a function of x in the whole x range, as typically shown for the unit-cell volume in Fig. 1(b). Thus, we have obtained a series of all proportional solid solution samples with varying Sb/Bi ratio. The electrical resistivities for x = 0, 0.10 and 0.20 show upturns due to CDW transitions, while the x = 0.30 sample shows a smooth temperature dependence (Fig. 2a). The transition temperature TCDW is determined from the temperature derivative of the resistivity curve, which decreases gradually with increasing x (Fig. 2b).

![Figure 2](image-url) Evolution of (a) resistivity curves and (b) their temperature derivatives for the solid solution BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O with x = 0, 0.10, 0.20 and 0.30.

At low temperatures, the resistivities show abrupt drops to zero at around 5.6 K except for x = 0, which may be due to the superconducting impurity phase of BaBi$_3$ with TC = 5.6 K [14]; the amount of BaBi$_3$ in the samples must be small as it is not detected in the XRD patterns of Fig. 1(a), but a superconducting path may be generated in a filament. Superconducting transitions of the bulk nature are detected by magnetic susceptibility and heat capacity measurements. Figure 3 shows the temperature dependences of magnetic susceptibility down to 1.8 K for 0.10 ≤ x ≤ 0.30 and 0.60 ≤ x ≤ 1. Large diamagnetic signals due to superconducting transitions are observed in the zero-field cooling curves for all the samples. The shielding volume fractions exceed 40% at the lowest temperature, indicating of the
bulk nature of the superconducting transitions. A small diamagnetic signal of 0.1% or less in volume fraction was also observed at 5.6 K from the impurity BaBi. The $T_c$s of BaTi$_3$(Sb$_{1-x}$Bi)$_2$O are determined at the onsets; 2.4 K ($x = 0.10$), 3.6 K (0.20), 2.6 K (0.30), 4.5 K (0.60), 4.5 K (0.70), 4.6 K (0.80) and 4.65 K (1). In contrast, no superconducting signals are observed above 1.8 K for $0.30 < x < 0.60$. The observed $x$ dependence of $T_c$ is consistent with that in the previous study [11].

![Figure 3](image)

**Figure 3.** Magnetic susceptibility for (a) $x = 0.1$, $0.2$, $0.3$ and (b) $x = 0.6$, $0.7$, $0.8$, $1$. Each measurement was carried in a magnetic field of 5 Oe upon heating after zero-field cooling and then upon cooling in the field.

In order to investigate the missing window of superconductivity at $0.30 < x < 0.60$, we have performed heat capacity measurements down to 0.5 K. Figure 4 shows the electronic heat capacity divided by temperature, $C_e/T$, for the samples with $x = 0.35$, $0.40$, $0.45$, $0.50$ and $0.55$, which were obtained after the subtraction of the lattice contribution. For all the samples, distinct but broad peaks are observed, indicating superconducting transitions in bulk at low temperatures. The $T_c$s are estimated on the basis of the entropy conservation for the broad transitions, as typically shown for $x = 0.50$ in Fig. 4(b): 1.45 K ($x = 0.35$), 1.0 K (0.40), 0.95 K (0.45), 0.88K (0.50) and 0.88 K (0.55). The magnitude of the jump at $T_c$, $\Delta C_e(T_c)/\gamma T_c$, is 0.45 for $x = 0.50$, which is significantly smaller than the weak-coupling BCS value of 1.43. The small jump and the broad transition may be partly due to degradation of the samples during the measurements.

Thus obtained $T_{CDWS}$ and $T_c$s are plotted in the phase diagram of Fig. 5. The $T_{CDW}$ decreases gradually from 57 K at $x = 0$ to 40 K at $x = 0.20$ and seems to vanish at around $x = 0.30$ in the resistivity data; it is not clear at which composition the $T_{CDW}$ really goes to zero. On the other hand, the $T_c$ shows a peak at $x = 0.20$ and remains at ~1 K at $x = 0.4–0.55$. Then, surprisingly, it shows a sudden jump to 4.5 K at $x = 0.60$ and remains nearly constant to the Bi end. Note that the superconductivity is observed at $x = 0.4–0.55$ in contrast to the previous result [11]. Moreover, it becomes clear that there is a discontinuous change in $T_c$ at $0.55 < x_c < 0.60$. 
Figure 4. (a) Electronic heat capacity divided by temperature down to 0.5 K for $x = 0.35, 0.40, 0.45, 0.50$ and 0.55. (b) $x = 0.50$ data.

The double $T_c$ dome of BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O is reminiscent of the similar double dome of LaFeAs(O$_{1-x}$H$_x$) [6]. The first peak at smaller $x$ values is no doubt related to the adjacent CDW order: its suppression by the Bi substitution must cause the $T_c$ peak, although it is not clear whether the CDW phase competes with or helps the superconductivity. In contrast, the presence of the superconductivity at $x \geq 0.6$ seems not to have such a parent ordered phase. Alternatively, one might assume that there is a dip at $x = 0.4$–0.55 in the single $T_c$ dome spreading over the whole $x$ range. In this case, the dip could be introduced as a consequence of the stabilization of a certain competing order, as in the case of La$_{2-x}$Ba$_x$CuO$_4$ [4].

Figure 5. Phase diagram of BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O. The CDW transition temperatures $T_{CDW}$ determined from the resistivity data are plotted by the triangles, and the superconducting transition temperatures $T_c$ from the magnetic susceptibility and heat capacity data are shown by open and filled circles, respectively.
Finally, we would like to consider the origin of the sudden jump of $T_c$ at $x_c$. Note that the two end members of BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O are structurally and electronically quite similar to each other. Their crystal structures at room temperature are basically the same, and no anomaly has been observed upon cooling in the solid solution. Thus, it is unlikely to assume a structural transition at $x_c$ to cause the $T_c$ jump, as in the cases of Au$_{1-x}$Pd$_x$Te$_2$ and Ca(Fe$_{1-y}$Rh$_y$)$_2$As$_2$ [15,16]. On the other hand, the electronic structures of the two end members also resemble each other, having similar Fermi surfaces [17], which make one believe the absence of a drastic change in the electronic structures at $x_c$ by the isovalent substitution. Further experiments are required for understanding this interesting phase diagram of BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O.

4. Summary
The electronic phase diagram of the titanium oxypnictide superconductor BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O is studied. It is found that the $T_c$ exhibits a double dome with a dip at $0.3 < x < 0.6$ and a sudden jump at $0.55 < x_c < 0.60$.

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