Superconducting properties of $\text{BaTi}_2\text{Pn}_2\text{O}$ ($\text{Pn} = \text{Sb}, \text{Bi}$)

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Abstract

We investigated superconducting (SC) properties of two layered titanium oxy pnictides $\text{BaTi}_2\text{Sb}_2\text{O}$ ($T_c = 1.2 \text{ K}$) and $\text{BaTi}_2\text{Bi}_2\text{O}$ ($T_c = 4.6 \text{ K}$) being located in distinct SC phases in $\text{BaTi}_2(\text{Sb}_{1-x}\text{Bi}_x)_2\text{O}$ by means of magnetic field dependence of electrical resistivities and magnetic susceptibilities. The SC parameter $H_{c2}(0)$ and ξ_0 for $\text{BaTi}_2\text{Sb}_2\text{O}$ are determined to be 1.32 T and 158 Å. For $\text{BaTi}_2\text{Bi}_2\text{O}$, we obtained $H_{c1}(0) = 0.006 \text{ T}$, $H_{c2}(0) = 1.70 \text{ T}$, $\lambda_0 = 2900 \text{ Å}$, $\xi_0 = 139 \text{ Å}$, and $\kappa = 20.8$. The density of states (DOS) for $\text{BaTi}_2\text{Bi}_2\text{O}$ at the Fermi level (4.79 states/eV/f.u.) is smaller than that for $\text{BaTi}_2\text{Sb}_2\text{O}$ (5.7 states/eV/f.u.). The DOS change by the Bi-for-Sb substitution is in accordance with theoretical calculations but it cannot explain the enhanced T_c .

Keywords

Superconductivity, $\text{BaTi}_2\text{Pn}_2\text{O}$, d^1 square lattice, Critical fields H_{c1} and H_{c2}

1. Introduction

The layered pnictide oxides $\text{ATi}_2\text{Pn}_2\text{O}$ [$\text{A}^{2+} = (\text{Na}^+)_2, \text{Ba}^{2+}, (\text{SrF})_2^{2+}, (\text{SmO})_2^{2+}; \text{Pn}^{3-} = \text{As}^{3-}, \text{Sb}^{3-}$] are similar to high T_c cuprates in terms of crystal and electronic structures [1-3]. $\text{ATi}_2\text{Pn}_2\text{O}$ has a Ti_2O square lattice that adopts the anticonfiguration to

the CuO_2 square lattice in cuprates. The electronic configuration of Ti^{3+} ($3d^1$) in $\text{ATi}_2\text{Pn}_2\text{O}$ is complementary with respect to Cu^{2+} ($3d^9$) in undoped cuprates. $\text{ATi}_2\text{Pn}_2\text{O}$ are known to exhibit charge density wave (CDW) or spin density wave (SDW) instability. For example, $\text{BaTi}_2\text{As}_2\text{O}$ shows a CDW/SDW transition at $T_a = 200$ K [1]. We recently succeeded to synthesize a new compound $\text{BaTi}_2\text{Sb}_2\text{O}$ (Fig. 1) [4,5] and found superconductivity with the transition temperature T_c of 1.2 K. The anomaly at $T_a = 50$ K was ascribed to CDW (not SDW) [6,7]. Another new compound $\text{BaTi}_2\text{Bi}_2\text{O}$, where the CDW instability is absent, has an enhanced T_c of 4.6 K. It appears that suppression of the CDW state by the Pn^{3-} replacement in $\text{BaTi}_2\text{Pn}_2\text{O}$ from As, Sb, to Bi contributes to the emergence and stabilization of the superconducting phase. However, the study of the isovalent solid solutions of $\text{BaTi}_2(\text{As}_{1-x}\text{Sb}_x)_2\text{O}$ and $\text{BaTi}_2(\text{Sb}_{1-y}\text{Bi}_y)_2\text{O}$ has revealed a novel two dome structure in the electronic phase diagram, with superconducting phases appearing in $0.9 \leq x; y \leq 0.3$ and $0.6 \leq y \leq 1$ [8]. Such a two-dome structure cannot be accounted for simply by, e.g., the ionic size effect for Pn^{3-} ions. In this study, we investigated superconducting properties of $\text{BaTi}_2\text{Sb}_2\text{O}$ and $\text{BaTi}_2\text{Bi}_2\text{O}$ in order to find a clue behind superconductivity and the two-dome structure in $\text{BaTi}_2\text{Pn}_2\text{O}$.

2. Experimental

The polycrystalline samples of $\text{BaTi}_2\text{Sb}_2\text{O}$ and $\text{BaTi}_2\text{Bi}_2\text{O}$ were synthesized by the conventional solid-state reaction method. BaO (99.99%, Aldrich), Ti (99.9%, Kojundo Chemical), Sb (99.9%, Kojundo Chemical) and Bi (99.9%, Kojundo Chemical) were accurately weighed according to the stoichiometric ratio of $\text{BaTi}_2\text{Sb}_2\text{O}$ or $\text{BaTi}_2\text{Bi}_2\text{O}$, then mixed and pelletized in nitrogen-filled dry box. The pellet was

wrapped with tantalum foil, sealed in a quartz tube, and heated at 1000 °C for 50 h for BaTi₂Sb₂O, and 850 °C for 50 h for BaTi₂Bi₂O, followed by controlled cooling at a rate of 25°C/h to room temperature. Powder synchrotron X-ray diffraction (SXR) data were collected at SPring-8 BL02B2 ($\lambda = 0.948139$ Å for BaTi₂Sb₂O, 0.353894 Å for BaTi₂Bi₂O). The Rietveld refinements were conducted using the RIETAN-FP program. The magnetic susceptibility for BaTi₂Sb₂O and BaTi₂Bi₂O was measured as a function of temperature with a SQUID (Quantum Design, MPMS). The temperature dependence of the electrical resistivity ρ under magnetic field ranged from 0 T to 2 T was measured with a standard DC four-terminal method using a physical property measurement system (Quantum Design, PPMS). Prior to the measurements, the powder samples were sintered at 500 °C in an evacuated Pyrex tube. Since BaTi₂Bi₂O is highly air- and moisture-sensitive, the sintered pellet of BaTi₂Bi₂O was coated by epoxy after contacting electrode.

3. Results and Discussion

The refined SXR patterns of BaTi₂Sb₂O and BaTi₂Bi₂O are shown in Figure 2. The sample of BaTi₂Bi₂O contains tiny amount of impurity phases Bi and BaO, whereas the BaTi₂Sb₂O specimen is a single phase. The inset of Figure 2 shows the magnetic susceptibility of BaTi₂Sb₂O and BaTi₂Bi₂O, where superconducting transitions are observed at 1.2 K and 4.6 K, respectively. These values are consistent with our previous results.

The magnetic field dependences of the electrical resistivity for BaTi₂Sb₂O and BaTi₂Bi₂O are shown in Figures 3(a) and 3(b). At zero magnetic field, the observed superconducting transition temperatures well agree with those of reported. In both

samples, we can suppress superconducting transitions by applying magnetic field. Figure 3(c) shows the temperature dependence of the upper critical field H_{c2} for BaTi₂Sb₂O and BaTi₂Bi₂O, as determined from the midpoint of the resistive transition. The residual resistivity of both samples is relatively high, suggesting that the samples are in the dirty limit. Interestingly, however, H_{c2} increased almost linearly with decreasing temperature down to the lowest temperature measured. We tentatively estimated H_{c2} at 0 K, $H_{c2}(0)$, from the linear extrapolation of the data and obtained 1.32 T for BaTi₂Sb₂O and 1.70 T for BaTi₂Bi₂O. Using $\mu_0 H_{c2}(0) = \Phi_0/2\pi\xi_0^2$ where Φ_0 is the magnetic flux quantum, the coherence length ξ_0 for BaTi₂Sb₂O and BaTi₂Bi₂O were estimated to be 158 Å and 139 Å, respectively.

The field dependence of the zero-field cooled magnetization at various temperatures for BaTi₂Bi₂O was shown in Figure 4(a). The H_{c1} was plotted as a function of $(T/T_c)^2$ in Figure 4(b). H_{c1} was fitted by Ginzburg Landau theory, $H_{c1}(T) = H_{c1}(0)[1-(T/T_c)^2]$, where $T_c = 4.6$ K was used. We obtained $H_{c1}(0)$ of 60 Oe and the penetration depth λ_0 of 2900 Å using $\mu_0 H_{c1}(0) = (\Phi_0/4\pi\lambda_0^2)\ln(\lambda_0/\xi_0)$ for BaTi₂Bi₂O. Using the relation $\kappa = \lambda_0/\xi_0$ and $\mu_0 H_c(0) = \Phi_0/(2\sqrt{2}\pi\xi_0\lambda_0)$, the Ginzburg-Landau parameter κ and the thermodynamic critical field $H_c(0)$ were determined as 20.8 and 577 Oe. For BaTi₂Sb₂O, we could not determine $H_{c1}(0)$ because of the lack of $H_{c1}(T)$ due to instrumental limits.

The higher T_c of BaTi₂Bi₂O (vs. BaTi₂Sb₂O) may come from the enhanced density of states at the Fermi energy $D(\epsilon_F)$ as a result of the complete suppression of CDW in BaTi₂Bi₂O. Since heat capacity data for BaTi₂Bi₂O is not available because of extreme air and moisture sensitivity, $D(\epsilon_F)$ and $\Delta(0)$ were estimated from the equation for weak-coupling limit, $[\mu_0 H_c(0)]^2/8\pi = D(\epsilon_F)\Delta(0)^2/2$ and $\Delta(0) = 1.764k_B T_c$, where $\Delta(0)$

is a superconducting gap. We obtained $D(\varepsilon_F) = 4.79$ states/eV/f.u. and $\Delta(0) = 0.70$ meV. For $\text{BaTi}_2\text{Sb}_2\text{O}$, $D(\varepsilon_F)$ was estimated to be 5.7 states/eV/f.u. using $\gamma = \pi^2 D(\varepsilon_F) k_B^2/3$ (where $\gamma = 13.5$ mJ/mol·K² [4]). These results indicate that $\text{BaTi}_2\text{Bi}_2\text{O}$ has smaller $D(\varepsilon_F)$ than $\text{BaTi}_2\text{Sb}_2\text{O}$, which is rather surprising as the former compound has no CDW instability and T_c is approximately four times as high as that for the latter. The decrease in $D(\varepsilon_F)$ by the Bi-for-Sb replacement was theoretically suggested: 4.26 states/eV/f.u. for $\text{BaTi}_2\text{Sb}_2\text{O}$ and 3.42 states/eV/f.u. for $\text{BaTi}_2\text{Bi}_2\text{O}$ [9,10], indicating the necessity to consider other reasons for the enhanced T_c in $\text{BaTi}_2\text{Bi}_2\text{O}$. Besides $D(\varepsilon_F)$, other factors like Debye temperature and electron-phonon coupling are known to provide influence on T_c . Given the isostructural nature of these compounds, the substitution of the heavier Bi element is expected to result in the similar or slightly smaller Debye temperature. Thus, the enhanced T_c in $\text{BaTi}_2\text{Bi}_2\text{O}$ could not be explained in the weak-coupling limit, indicating the increased electron-phonon coupling by the change in the Fermi surface may be responsible for the enhanced T_c .

The electronic phase diagram of isovalent pnictide solid solutions of $\text{BaTi}_2\text{Pn}_2\text{O}$ shows the presence of two superconducting phases, which strongly indicates a multiband nature at the Fermi surface. The contribution of several Ti 3d orbitals and Pn p orbitals to $D(\varepsilon_F)$ is theoretically addressed (although the two-dome structure is not reproduced). In addition, the metallic phase separating the two superconducting states does not show any CDW/SDW instabilities at low temperatures [8]. Therefore, a difference in Fermi surface between $\text{BaTi}_2\text{Sb}_2\text{O}$ and $\text{BaTi}_2\text{Bi}_2\text{O}$ may provide significant influence on the electron-phonon interaction and changes T_c .

4. Summary

We performed electrical resistivity and magnetic susceptibility measurements under various magnetic field for novel superconductors $\text{BaTi}_2\text{Sb}_2\text{O}$ ($T_c = 1.2$ K) and $\text{BaTi}_2\text{Bi}_2\text{O}$ ($T_c = 4.6$ K). Superconducting parameters $H_{c1}(0)$, $H_{c2}(0)$, λ_0 , ξ_0 , and κ for $\text{BaTi}_2\text{Bi}_2\text{O}$ were determined to be 0.006 T, 1.70 T, 2900 Å, 139 Å, and 20.8, respectively. In accordance with theoretical prediction, the density of states estimated from these parameters in $\text{BaTi}_2\text{Bi}_2\text{O}$ (4.79 states/eV/f.u.) is smaller than that obtained in $\text{BaTi}_2\text{Sb}_2\text{O}$ (5.7 states/eV/f.u.). Given two superconducting phases in the electronic phase diagram of $\text{BaTi}_2\text{Pn}_2\text{O}$, the present results imply that the origin of superconductivity in $\text{BaTi}_2\text{Sb}_2\text{O}$ and $\text{BaTi}_2\text{Bi}_2\text{O}$ is different from each other.

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Figure captions

Figure 1.

Crystal structure of $\text{BaTi}_2Pn_2\text{O}$ ($Pn = \text{Sb, Bi}$).

Figure 2.

Refined synchrotron X-ray diffraction pattern of (a) $\text{BaTi}_2\text{Sb}_2\text{O}$ and (b) $\text{BaTi}_2\text{Bi}_2\text{O}$, showing observed (red circle), calculated (green line), and difference (blue line) profiles. The green ticks in (a) represent the position of the calculated Bragg reflections of $\text{BaTi}_2\text{Sb}_2\text{O}$. The upper, middle and lower ticks in (b) represent positions of the calculated Bragg reflections of $\text{BaTi}_2\text{Bi}_2\text{O}$, Bi, and BaO, respectively. The insets show their magnetic susceptibilities at low temperatures.

Figure 3.

The electrical resistivity for (a) $\text{BaTi}_2\text{Sb}_2\text{O}$ and (b) $\text{BaTi}_2\text{Bi}_2\text{O}$ under various magnetic fields as a function of temperature. (c) The temperature dependence of H_{c2} for $\text{BaTi}_2\text{Sb}_2\text{O}$ and $\text{BaTi}_2\text{Bi}_2\text{O}$.

Figure 4.

(a) Magnetic field dependence of magnetization for $\text{BaTi}_2\text{Bi}_2\text{O}$ at various temperatures. (b) The lower critical field H_{c1} for $\text{BaTi}_2\text{Bi}_2\text{O}$ as a function of $(T/T_c)^2$.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4