Weak coupling BCS-like superconductivity in the pnictide oxide $Ba_{1-x}Na_xTi_2Sb_2O$ ($x = 0$ and 0.15)

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We report the results of low-temperature heat capacity measurements of the pnictide oxide superconductor $BaTi_2Sb_2O$ doped with sodium. The temperature- and field-dependent heat capacity data are well described by a single-gap BCS theory. The estimated values for the normal-state Sommerfeld constant, the heat capacity jump at T_c, and the electron-phonon coupling constant are in favor of a conventional weak coupling superconductivity mediated by electron-phonon interaction. The results are discussed with regard to and compared with recent first-principles calculations.

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I. INTRODUCTION

Superconductivity in layered transition-metal compounds has been in the focus of interest for several decades. The discovery of high-temperature superconductivity in copper oxide perovskites as well as, more recently, in iron pnictides and chalcogenides has initiated an immense activity in superconductivity research. Questions about the role of the layered structure, magnetic fluctuations, the proximity to magnetic order or a possible quantum critical point, the symmetry of the superconducting order parameter, etc. have been discussed extensively. There are numerous examples showing that the superconducting state, usually induced by carrier doping into a parent compound, is in close proximity to spin or charge orders, for example antiferromagnetic order in copper oxide and heavy-fermion superconductors, spin-density-wave (SDW) order in iron pnictides, or charge-density-wave (CDW) order in layered chalcogenides.[1–5] The mutual interactions of different fundamental orders open new perspectives to study novel physical phenomena observable only in those strongly correlated superconducting systems.

The search for similar layered transition-metal compounds has recently led to the study of titanium-based pnictide oxide compounds of the general chemical formulas $A_2Ti_2Pn_2O$ and $AeTi_2Pn_2O$ (Pn = As,Sb; A = Na; Ae = Ba). This system was first synthesized and characterized more than two decades ago[6] and it belongs to a larger family of pnictide oxides including other transition metals.[7–9] The layered structure of $Na_2Ti_2Pn_2O$ is characterized by Ti_2Pn_2O blocks separated by a double layer of A (Na) ions or single slabs of Ae (Ba). The titanium and oxygen ions form square planar Ti_2O sheets, which is inverse (anti) to the CuO_2 planes which form the active layer in superconducting copper oxides, in that the positions of Ti and O in this square lattice are switched with respect to the O and Cu sites in the cuprates. This raised the question of whether or not a superconducting state can be induced through doping of carriers into the Ti_2O layer.[8]

The structure and chemical synthesis of $Na_2Ti_2Pn_2O$ have been studied in detail for Pn = As and Sb.[6,10,11] The physical properties studied via electrical transport and magnetic measurements reveal the existence of an instability near T_{DW} = 115 K in $Na_2Ti_2Sb_2O$ where the magnetic susceptibility shows a sharp drop to lower values and the resistivity experiences a sudden increase.[11–13] However, it is not clear if this instability originates from the formation of a charge-density wave or a spin-density wave. First-principles calculations have found a nesting feature of the Fermi surface which could explain the occurrence of a SDW or CDW instability.[14] Powder neutron scattering experiments have shown that this transition is also associated with a small structural anomaly.[10] Recent optical studies have found the opening of a gap and a change of the free-carrier spectral weight as well as a reduction of the carrier scattering rate across the SDW-CDW transition.[15] It is worth noting that the arsenic-based compound, $Na_2Ti_2As_2O$ exhibits a similar density-wave transition at significantly higher temperature, T_{DW} = 320 K.[13]

Replacing the Na_2 double layer with a single layer of Ba ions forms another stable pnictide oxide, $BaTi_2As_2O$, with the c axis of the tetragonal structure shortened by 50%.[16] Interestingly, this compound features identical Ti_2As_2O layers and it also exhibits the density-wave transition at T_{DW} = 200 K, albeit significantly lower than in the related compound $Na_2Ti_2As_2O$. However, attempts to induce superconductivity in $BaTi_2As_2O$ through doping or intercalation have not been successful.[16]

Replacing As by Sb and forming $BaTi_2Sb_2O$ was achieved only very recently.[17,18] Superconductivity was observed below 1.2 K,[18] and the critical temperature could be raised to above 5 K through Na doping at the Ba site in $Ba_{1-x}Na_xTi_2Sb_2O$.[17] The undoped parent compound shows a density-wave transition at much lower temperature, T_{DW} = 54 K, and it was shown that Na doping decreased the critical temperature even further (while raising the superconducting T_c).[17] The questions about the nature of the superconducting state and whether or not the density-wave state competes or supports superconductivity are yet to be explored.

Electronic structure calculations by Singh[19] have shown the existence of several sheets at the Fermi surface and a nesting property which induces a magnetic instability (SDW). Related to this instability, a sign-changing s-wave state was predicted to originate from an unconventional spin-fluctuation-mediated superconductivity. The coupling of charges to the magnetic order is observed in a strong magnetoresistance effect below T_{DW} in $BaTi_2Sb_2O$,[17] as well as in $BaTi_2As_2O$.[16]

On the other hand, Subedi[20] suggested the electron-phonon mechanism for superconductivity and a CDW instability in $BaTi_2Sb_2O$ based on first-principles calculations of the phonon dispersions and electron-phonon interactions, predicting a multiband superconducting state, similar to some iron pnictide superconductors.

To distinguish between different proposals about the microscopic origin of superconductivity in $Ba_{1-x}Na_xTi_2Sb_2O$ experimental probes on the superconducting gap structure need to be employed. The temperature dependence of the electronic heat capacity $C_{el}(T)$ measured to low temperatures is a sensitive probe which can reveal unconventional superconductivity, the existence of nodes in the superconducting gap function, and the possible presence of multiple gaps (multiband superconductivity). We have therefore studied the heat capacity of $Ba_{1-x}Na_xTi_2Sb_2O$ in applied magnetic fields and at temperatures as low as 0.4 K. Our results are consistent with a single-gap weak coupling BCS-like superconducting state.

II. EXPERIMENT

High-purity polycrystalline samples of $BaTi_2Sb_2O$ were synthesized by reacting stoichiometric amounts of BaO (99.99% Aldrich) and Ti (99.99% Aldrich), and Sb pieces (99.999%, Alfa Aesar) in welded niobium containers within evacuated quartz jackets. The well-mixed reactants were pressed into pellets and then sealed in niobium tubes under argon and subsequently jacketed, evacuated, and sealed in quartz tubes. The samples were heated slowly (2°C/min) to 900°C and annealed for 3 days, then slowly cooled (1°C/min) to 200°C. To ensure phase homogeneity, an additional regrinding and sintering at 900°C for another 3 days was performed. $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$ was synthesized by reacting stoichiometric amounts of BaO (99.99%, Sigma Aldrich), BaO_2 (95%, Sigma Aldrich), Na_2O (80% Na_2O and 20% Na_2O_2, Sigma Aldrich), Ti (99.99%, Sigma Aldrich), and Sb (pieces, 99.999%, Alfa Aesar) in welded niobium containers within evacuated quartz jackets. The major impurity in Na_2O (20% Na_2O_2) had to be taken into account during the weighing. The well-mixed reactants were pressed into pellets and sealed in niobium tubes under argon, and subsequently jacketed, evacuated, and sealed in quartz tubes. The samples was heated slowly (2°C/min) to 900°C and annealed for 3 days, then slowly cooled (1°C/min) to 200°C. As for $BaTi_2Sb_2O$, an additional regrinding and sintering at 900°C for another 3 days was performed to ensure phase homogeneity. The phase purity of the samples was investigated through powder x-ray diffraction, as well as through inductively coupled plasma–mass spectrometry (ICP-MS). ICP-MS confirmed the Ba:Na molar ratio to be close to the nominal composition, as reported earlier.[17] To prevent contamination of the air- and moisture-sensitive material all preparations had to be performed in an argon glovebox. The magnetic properties were measured using a magnetic property measurement system (Quantum Design) and the heat capacity data were collected using a relaxation method and the ^{3}He probe attached to the physical property measurement system (Quantum Design). Four-probe resistivity measurements were carried out in the physical property measurement system ^{3}He probe using an external LR700 (Linear Research) low-frequency (19 Hz) ac bridge. Measurements were carried out to temperatures as low as 0.4 K and in magnetic fields up to 70 kOe.

III. RESULTS AND DISCUSSION

The superconducting transition for $BaTi_2Sb_2O$ and $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$ is clearly indicated in Figs. 1(a) and 1(b). The $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$ superconducting transition is seen in Fig. 1(a), by the diamagnetic signal with onset below 5 K. This transition is also confirmed through resistivity data, as seen in Fig. 1(b), with the midpoint of the transition occurring at 5 K. Figure 1(b) also shows resistivity data for $BaTi_2Sb_2O$. The superconducting transition is very sharp and the midpoint of the transition is at 1.2 K. The sharpness of the transition is an indication of the high purity of the sample, which is further revealed by a high residual resistance ratio of about 40, significantly higher than in previous reports.[18,21]

The heat capacity data of $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$ are shown in Fig. 2. The superconducting state is completely suppressed in a magnetic field of 30 kOe. From the high-field data the

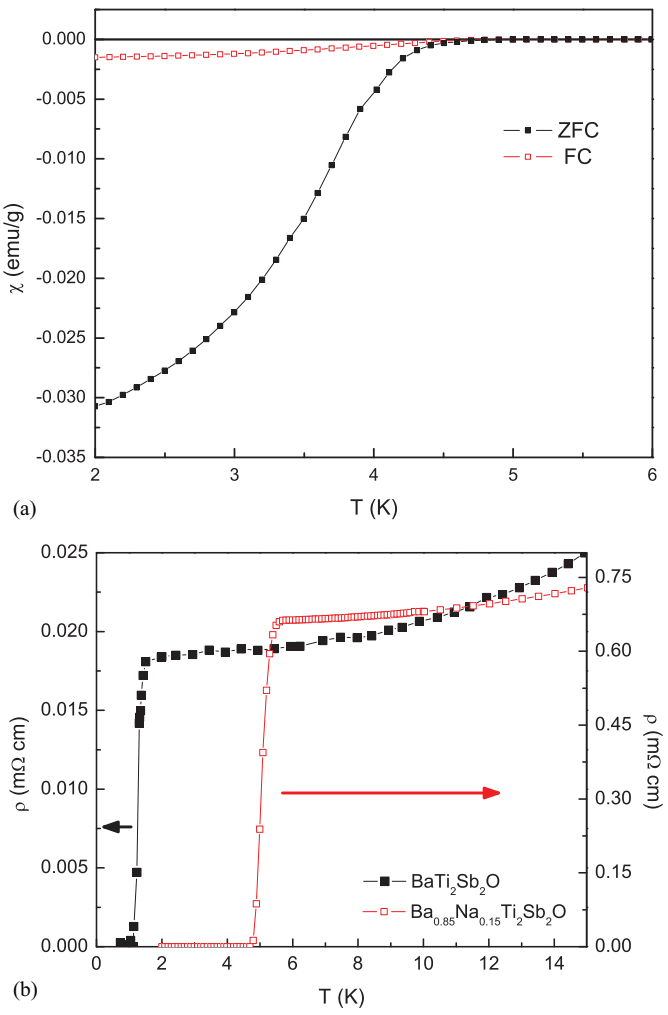

FIG. 1. (Color online) (a) Magnetic susceptibility $\chi(T)$ of $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$ measured in field-cooling (FC) and zero-field-cooling (ZFC) conditions. (b) Resistivity of $BaTi_2Sb_2O$ and $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$.

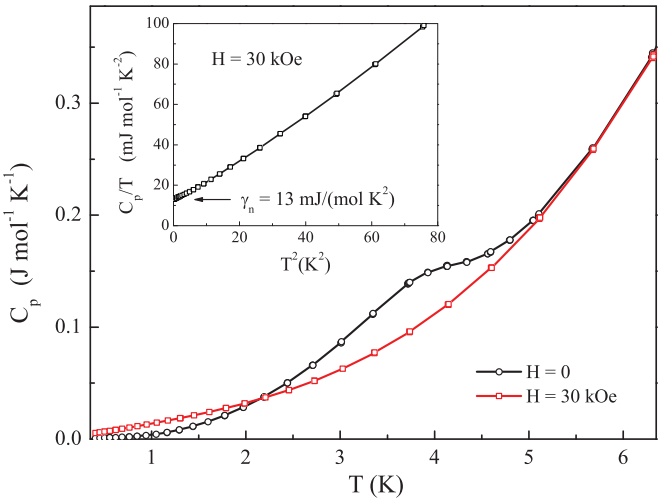

FIG. 2. (Color online) Heat capacity of $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$ measured in zero field and at 30 kOe (above H_{c2}). The inset shows the normal state heat capacity C_p/T vs. T^2 (30 kOe) data). The Sommerfeld constant is determined as $\gamma_n = 13$ mJ/(mol K^2).

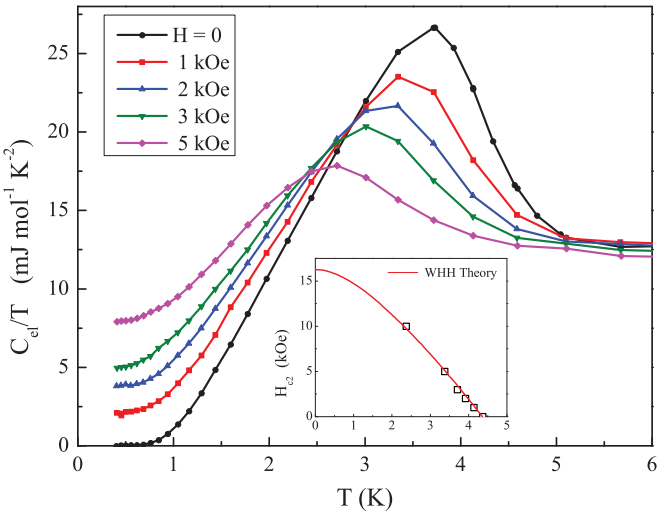

FIG. 4. (Color online) Magnetic field dependence of the electronic heat capacity C_{el}/T of $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$. The inset shows the upper critical field $H_{c2}(T)$ and the curve expected from the WHH theory.

normal-state Sommerfeld constant is obtained as $\gamma_n = 13$ mJ/(mol K^2). However, it should be noted that this value for γ_n is enhanced by the electron-phonon coupling constant, as discussed below, and the bare electronic value relating to the density of states is lower.

The electronic heat capacity $C_{el}(T)$ was derived from the data shown in Fig. 2 by subtracting the lattice contribution determined from the high-field data. The resulting data for the normalized $C_{el}/(\gamma_n T)$ are very well described by a weak coupling BCS function, shown as the dashed line in Fig. 3. The excellent agreement of the data with the BCS theory is evidence for conventional superconductivity in the pnictide oxide family of compounds. In addition, we do not find any signature of a possible multiband superconducting state which would leave the typical imprint on the low-temperature part of the heat capacity as, for example, observed in MgB_2.[22,23] The superconducting gap value is estimated as $2\Delta = 1.3$ meV.

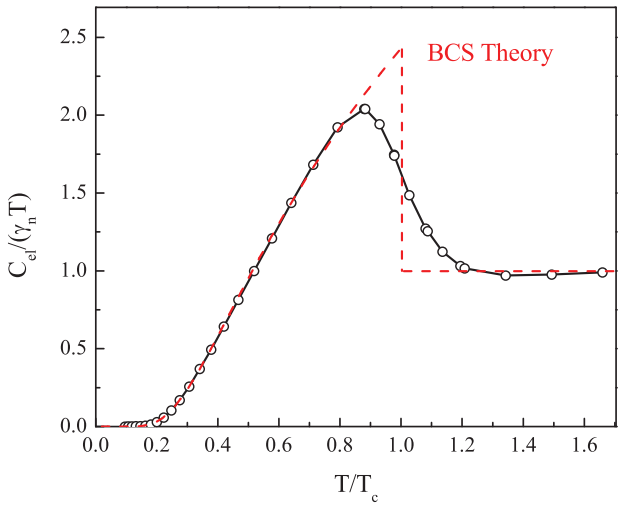

FIG. 3. (Color online) Normalized electronic heat capacity $C_{el}/(\gamma_n T)$ of $Ba_{0.85}Na_{0.15}Ti_2Sb_2O$ measured in zero field. The dashed line represents the heat capacity from weak coupling BCS theory.

The magnetic field dependence of $C_{el}(T)$ is shown in Fig. 4. The upper critical field $H_{c2}(T)$ is extracted from the shift of T_c in magnetic fields, with T_c defined as the midpoint of the sharp increase of $C_{el}(T)$. $H_{c2}(T)$ is shown in the inset of Fig. 4 and compared with the Werthamer-Helfand-Hohenberg (WHH) theory[24] (line). The zero-temperature limit of the critical field is extrapolated as $H_{c2}(0) = 17$ kOe, which results in a Ginzburg-Landau coherence length of $\xi(0) = 14$ nm.

The superconducting transition in the undoped $BaTi_2Sb_2O$ happens at significantly lower temperature. However, the very broad transition reported originally[18] provides a challenge for a detailed analysis of the low-temperature heat capacity. Our samples of $BaTi_2Sb_2O$ were prepared with special care to reduce any impurity or defect content to a minimum.[17] As a result, a very sharp resistive transition at $T_c = 1.2$ K (transition width <0.2 K) and also at T_{DW} was observed as well as a much sharper heat capacity change at T_c. The zero-field normalized electronic heat capacity $C_{el}/(\gamma_n T)$ of $BaTi_2Sb_2O$ is shown in Fig. 5 as a function of the normalized temperature T/T_c. In contrast to the Na-doped compound discussed above, the BCS theory (dashed line in Fig. 5) does not fit the data well. By varying the superconducting gap size while maintaining the BCS-like temperature dependence of the gap (the so-called α model[25]) a much better fit is obtained with $\alpha \approx 1.4$ (solid line in Fig. 5). These data still support a single-gap s-wave superconductivity with a gap value of $2\Delta = 0.3$ meV, consistent with conclusions from recent NMR measurements.[26] Interestingly, the heat capacity jump at T_c is only 0.9 of the normal-state value, much smaller than 1.43 (BCS theory) or 1.36 (Yajima *et al.*[18]). This low value may suggest strong correlations, possibly related to the ordered density-wave phase below T_{DW}. The Sommerfeld coefficient $\gamma_n = 10.9$ mJ/(mol K^2) is about 20% lower than reported earlier,[18] which we attribute to differences in sample purity.

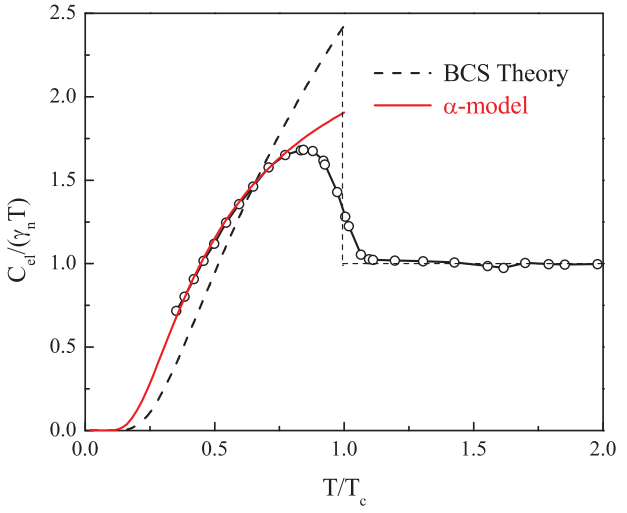

FIG. 5. (Color online) Normalized electronic heat capacity of $BaTi_2Sb_2O$ at zero magnetic field. The BCS data are shown by the dashed line. The experimental data fit well to the α model (with $\alpha \approx 1.4$).

The heat capacity peak in magnetic fields shows the expected shift to lower temperatures; however, the upper critical field is very low. Figure 6 shows heat capacity data for $BaTi_2Sb_2O$ in external fields up to 500 Oe. The upper critical field $H_{c2}(T)$ is shown in the inset of Fig. 6. The extrapolation to zero temperature, using the WHH theory, results in a very low value of $H_{c2}(0) \approx 800$ Oe and a coherence length of $\xi(0) = 64$ nm.

Assuming that the origin of the single-gap superconducting state lies in the electron-phonon coupling mechanism, as suggested by Subedi,[20] the coupling constant λ_{ep} and the bare electronic Sommerfeld constant γ_0 can be estimated from the McMillan formula for λ_{ep} (Ref. 27) and the relation $\gamma_n = \gamma_0(1 + \lambda_{ep})$. With an assumed value of $\mu^* = 0.13$, the results for $x = 0$ and $x = 0.15$ are summarized in Table I. The Na doping results in a moderate increase of

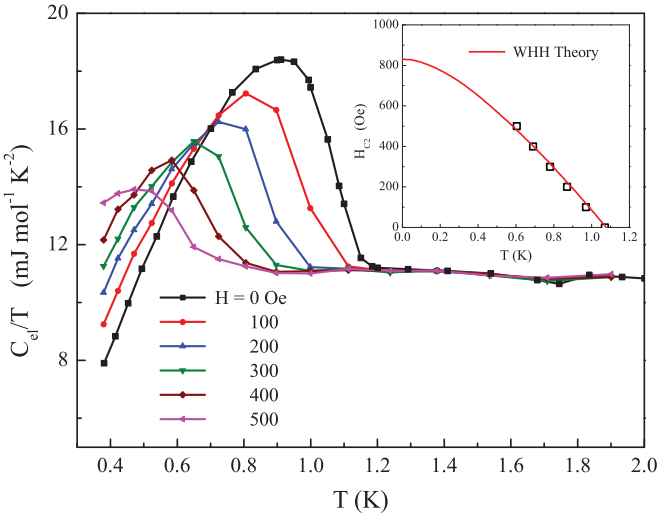

FIG. 6. (Color online) Magnetic field dependence of the electronic heat capacity C_{el}/T of $BaTi_2Sb_2O$. The inset shows the upper critical field $H_{c2}(T)$ and the curve expected from the WHH theory.

TABLE I. Superconducting- and normal-state parameters of $Ba_{1-x}Na_xTi_2Sb_2O$. The units of γ_n and γ_0 are mJ/(mol K^2).

x	T_c (K)	H_{c2} (kOe)	$\xi(0)$ (Å)	Θ_D (K)	λ_{ep}	γ_n	γ_0
0	1.1	0.8	640	230	0.49	10.9	7.3
0.15	4.2	17	140	210	0.68	13.0	7.7

the density of states (as derived from the increase of γ_0 by about 5%); however, the electron-phonon coupling constant increases significantly by almost 40%, resulting in the four times higher value of T_c. However, it should be noted that this discussion is based solely on the assumption that the pairing mechanism is via the electron-phonon interaction,[20] but alternative possibilities, e.g., spin-fluctuation-mediated pairing as suggested by Singh,[19] cannot be ruled out.

IV. CONCLUSION

The heat capacity data for $BaTi_2Sb_2O$ and $Ba_{1-x}Na_xTi_2Sb_2O$ are best described by a single-gap BCS function in the weak coupling limit. This provides evidence that the superconductivity in this compound is most likely of s-wave character, as was also implied from nuclear magnetic and quadrupole resonance measurements of the undoped compound.[26] The question of whether the pairing is mediated by phonons or spin fluctuations is yet unresolved. The key seems to be the understanding of the nature of the density-wave order below T_{DW}.

All theoretical studies so far agree about the nesting feature of the Fermi surface of $Na_2Ti_2Sb_2O$ (Refs. 14 and 28) and $Ba_{1-x}Na_xTi_2Sb_2O$ (Ref. 19) which is most likely the origin of the density-wave order. This order coexists with superconductivity in $Ba_{1-x}Na_xTi_2Sb_2O$ ($0 \leqslant x \leqslant 0.33$).[17,18,26] While this density-wave order has been observed earlier in different pnictide oxides like $Na_2Ti_2As_2O$ ($T_{DW} = 320$ K),[13] $Na_2Ti_2Sb_2O$ ($T_{DW} = 114$ K),[12] and $BaTi_2As_2O$ ($T_{DW} = 200$ K),[16] no superconductivity was found in these systems and attempts at doping or intercalation have not been successful.[16] The superconductivity in $Ba_{1-x}Na_xTi_2Sb_2O$ appears in the compound with the lowest $T_{DW} \leqslant 54$ K, suggesting that density-wave and superconducting states are competing with one another. The decrease of T_{DW} and simultaneous increase of the superconducting T_c upon Na doping[17] support the latter conclusion. Furthermore, the recently reported superconductivity in the system $BaTi_2(Sb_{1-x}Bi_x)_2O$ also shows that the substitution of Bi for Sb results in a suppression of the density-wave phase and an increase of T_c.[21,29] Therefore, it is most likely that the superconducting state and the density-wave order compete, and superconductivity is possible only in pnictide oxide compounds with a lower energy scale of the DW phase. While our results suggest that the superconducting state is a conventional s-wave state, the nature of the pairing mechanism is unclear at this time and may be either induced by the electron-phonon coupling[20] or spin-fluctuation derived.[19] While no conclusion can be drawn on the pairing mechanism, we also have not found any evidence for a multiband character of the superconducting state in our heat capacity data.

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