Superconductivity, charge- or spin-density wave, and metal-nonmetal transition in BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O

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We have performed an isovalent substitution study in a layered titanium oxypnictide system BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O (0 ≤ x ≤ 0.40) by the measurements of x-ray diffraction, electrical resistivity and magnetic susceptibility. The parent compound BaTi$_2$Sb$_2$O is confirmed to exhibit superconductivity at 1.5 K as well as charge- or spin-density wave (CDW/SDW) ordering below 55 K. With the partial substitution of Sb by Bi, the lattice parameters a, c and c/a all increase monotonically, indicating a negative chemical pressure and lattice distortion for the (super)conducting Ti$_2$Sb$_2$O-layers. The Bi doping elevates the superconducting transition temperature to its maximum $T_c$=3.7 K at x =0.17, and then $T_c$ decreases gradually with further Bi doping. A metal-to-nonmetal transition takes place around x=0.3, and superconductivity at ~1 K survives at the nonmetal side. The CDW/SDW anomaly, in comparison, is rapidly suppressed by the Bi doping, and vanishes for x ≥0.17. The results are discussed in terms of negative chemical pressure and disorder effect.

PACS numbers: 74.70.Xa; 74.62.-c; 71.45.Lr; 75.30.Fv; 72.15.Rn

Superconductivity (SC) and charge- or spin-density wave (CDW/SDW, or abbreviated as DW) are different collective electronic phenomena in crystalline materials. The DW state often appears in low dimensional metallic system in which the Fermi surfaces (FSs) are nested, showing a real-space modulation of charges or spins. SC can be regarded as another kind of FS instability due to Cooper pairing, which exhibits an electronic ordering in momentum space in the form of condensation of Cooper pairs. While SC generally competes with DW, the coexistence of SC and DW is possible$^2$. In iron-based superconducting systems, SC emerges from$^3$, or may also coexist with$^4$, an antiferromagnetic SDW state, which arouse enormous and intensive researches$^5,6,7$.

A possible CDW/SDW anomaly has been observed in a class of titanium oxypnictides since 1990s$^5,8-11$. The material contains Ti$_2$O square lattice that was considered to play an important role for the anomaly$^{12,14}$. The Ti$_2$O sheets can be viewed as an analogue of CuO$_2$-planes in cuprate superconductors (if Cu and O atoms of the latter are replaced by O and Ti, respectively, Ti$_2$O lattice forms). Besides, the Ti valence is 3+, giving a d$^1$ configuration for Ti$^{3+}$, in contrast with the d$^9$ configuration for Cu$^{2+}$ in cuprates. Therefore, continuous efforts have been made to explore possible SC in these layered titanium oxypnictides$^{5,8,9,10}$. But it was not until very recently that SC was observed in the related systems. Sun et al.$^{15}$ observed SC at 21 K and DW anomaly at 125 K in an intergrowth compound Ba$_2$Ti$_2$Fe$_2$As$_4$O containing both Fe$_2$As$_2$ and Ti$_2$O layers. However, the SC was believed to stem from the Fe$_2$As$_2$-layers rather than the Ti$_2$O-sheets. Very recently, Yajima et al.$^{16}$ reported SC at 1.2 K as well as a DW transition at 50 K in BaTi$_2$Sb$_2$O. Doan et al.$^{17}$ found that, by the hole doping with sodium, the superconducting transition temperature, $T_c$, increased to 5.5 K. Meanwhile the DW transition temperature, $T_{DW}$, decreased to about 30 K. The result suggests competing interplay between SC and the DW ordering.

The new findings call for investigation of the nature of DW state and its relation to SC. Earlier neutron diffraction study of Na$_2$Ti$_2$Sb$_2$O$^{18}$ failed to observe any long-range magnetic ordering associated with the resistivity anomaly at 120 K. Instead, only a structural distortion in the Ti$_2$Sb$_2$O-layer was found. On the other hand, theoretical calculations$^{12,13}$ suggest nearly two-dimensional FS nesting that points to a DW instability. Recent first-principles calculations tend to favor SDW scenarios in BaTi$_2$As$_2$O$^{19}$, Ba$_2$Ti$_2$Fe$_2$As$_4$O$^{19}$, BaTi$_2$Sb$_2$O$^{20}$, Na$_2$Ti$_2$As$_2$O$_{21}$, and Na$_2$Ti$_2$Sb$_2$O$_{21}$. If the SC is in proximity to an SDW phase, unconventional SC mediated by spin fluctuations could be expected$^{20}$. Nevertheless, CDW instability was also supported by the calculations of phonon dispersions and electron-phonon coupling for BaTi$_2$Sb$_2$O$^{22}$.

Previous reports$^{7,8,11,16,17}$ suggest that $T_{DW}$ decreases remarkably when As$^{3-}$ is replaced by Sb$^{3-}$ accompanying with a lattice expansion. SC appears as DW is sufficiently suppressed$^{16,17}$. Therefore, it is of great interest to investigate the effect of isovalent substitution by the last pnictogen Bi in BaTi$_2$Sb$_2$O$^{23}$. In this paper, we present a systematic Bi-substitution study in the BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O (1221) system. As expected, the lattice is expanded by the partial substitution. $T_c$ increases up to 3.7 K at x=0.17, and concomitantly the DW anomaly is suppressed. Surprisingly, a metal-to-nonmetal transition takes place around x=0.3 where SC is still robust. The results suggest that the negative chemical pressure suppresses DW and enhances SC, and the concomitant disorder tends to destroy both DW and
SC in BaTi$_2$(Sb$_{1-x'}$Bi$_{x'}$)$_2$O.

Polycrystalline samples of BaTi$_2$(Sb$_{1-x'}$Bi$_{x'}$)$_2$O with nominal Bi content $x'=0$, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 were synthesized by solid state reaction in vacuum using the starting material of powders of BaO (Alfa Aesar, 99.5%), Ti (Alfa Aesar, 99.9%), Sb (Alfa Aesar, 99.5%) and Bi (Alfa Aesar, 99.5%). To obtain a dense pellet that favors the subsequent resistance measurement, intermediate products of "Ti$_3$Sb$_3$" and TiBi were prepared respectively at 923 K in an evacuated quartz tube for 24h. Then the stoichiometric mixtures of BaTi$_2$(Sb$_{1-x'}$Bi$_{x'}$)$_2$O were ground in an agate mortar, and pressed into pellets under a pressure of 2000 kg/cm$^2$, in a glove box filled with pure argon (the water and oxygen content was below 0.1 ppm). The pellets, wrapped with Ta foils, were sintered at 1323 K for 30h in a sealed evacuated quartz ampoule, followed by naturally cooling to room temperature. The as-prepared pellets were very sensitive to moist air. Exposure in ambient conditions for a few hours led to decomposition of the 1221 phase completely.

Powder x-ray diffraction (XRD) was carried out at room temperature using a PANalytical x-ray diffractometer (Model EMPYREAN) with a monochromatic CuK$_{\alpha_1}$ radiation. The lattice parameters were obtained by least-squares fit of more than 20 XRD reflections with the correction of zero shift, using space group of $P4/mmm$ as previously proposed. Energy dispersive x-ray spectroscopy (EDXS) on a single crystalline grain under a field-emission scanning electron microscope was used to determine the exact composition, especially for the incorporated Bi content. The measurement precision was within $\pm 5\%$ for the elements Ba, Ti, Sb and Bi.

Temperature-dependent resistivity was measured in a Cryogenic Mini-CFM measurement system by a standard four-terminal method. Additional resistivity measurements down to 0.5 K were carried out in a $^3$He refrigerator inserted in a Quantum Design PPMS-9 instrument. Gold wires were attached onto the samples’ newly-abraded surface with silver paint, keeping least exposure in air. The size of the contact pads leads to a total uncertainty in the absolute values of resistivity of $\pm 15\%$. Temperature-dependent dc magnetic susceptibility was performed on a Quantum Design MPMS-5 equipment. Both the zero-field-cooling (ZFC) and field-cooling (FC) protocols were employed under the field of 10 Oe for probing superconducting transitions. A magnetic field of $H=10\, kOe$ was applied for tracking the DW anomaly.

Samples of BaTi$_2$(Sb$_{1-x'}$Bi$_{x'}$)$_2$O were first characterized by powder XRD. Most of the XRD reflections can be well indexed by a tetragonal lattice, as depicted in the inset of figure 1(a), with $a \sim 4.11$ Å and $c \sim 8.10-8.20$ Å. Tiny metal Bi was segregated from the main 1221 phase for low-doping ($x' \leq 0.2$) samples, and the amount of Bi and BaTiO$_3$ impurities increases a little for the high-doping samples. With the Bi doping, the XRD peaks shift systematically[figure 1(b)], suggesting that most bismuth incorporates the lattice. The actual Bi content ($x$) in the 1221 phase was determined by EDXS which showed nearly 20\% less than the nominal value $x'$, depending on the doping levels and synthetic conditions. The result gives $x=0, 0.04, 0.08, 0.13, 0.17, 0.20, 0.25, 0.3, 0.35$, and 0.40 for the nominal $x'$ values of 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, and 0.45, respectively.

With the Bi substitution, the (200) reflections move minutely, but the (004) reflections shift remarkably, to the lower diffraction angles, consistent with the mild increase in $a$-axis, yet significant increase in $c$-axis [figure 1(c)]. The lattice expansion indicates a negative chemical pressure by the Bi substitution. Besides, the increase in $c/a$ ratio suggests structural distortions in Ti$_3$Sb$_2$O-layers. It was found that the fractional coordinate of each atom in the unit cell of Na$_2$Ti$_3$Sb$_2$O did not change with the lattice constants upon decreasing temperature. This means that the $c/a$ ratio is basically proportional to the ratio of Sb-height to Ti-O bondlength. The latter influences the crystal field splitting of the Ti 3$d$ orbitals that was linked with the DW instability. Since the $c/a$ ratio is significantly smaller for a DW state and furthermore the $c/a$ value is only
1.8 for BaTi$_2$As$_2$O whose $T_{DW}$ is as high as 200 K; the increase in $c/a$ would be unfavorable for the DW formation. As will be seen below, the DW ordering is indeed suppressed by the Bi doping.

Figure 2 shows temperature dependence of resistivity [$\rho(T)$] of the BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O polycrystalline samples. The $\rho(T)$ data of the undoped compound resemble those of previous reports with regard to the DW anomaly at $T_{DW} \sim 55$ K, but the absolute resistivity is about one order of magnitude smaller. The residual resistance ratio (RRR), conventionally defined by the ratio of room-temperature resistance and low-temperature one, is $\sim 20$, much higher than those of previous reports. This suggests high quality of the present samples. Upon Bi doping, $T_{DW}$ decreases monotonically, and it vanishes for $x \geq 0.17$. As stated above, suppression of the DW state may be interpreted in terms of increase of $c/a$ ratio associated with the negative chemical pressure.

In addition to the negative chemical pressure effect, the Bi doping induces disorder concomitantly. The low-temperature residual resistivity increases almost proportionally with $x$ in the low-doping regime. This can be explained by the conventional impurity scattering due to the Sb/Bi substitution disorder. For the high-doping samples, however, the absolute resistivity increases rapidly. The low-$T$ resistivity increases by three orders of magnitude from $x=0$ to $x=0.3$. Furthermore, the temperature coefficient of resistivity (TCR) changes sign at $x \sim 0.3$, pointing to a metal-to-nonmetal (M-NM) transition. The origin of the M-NM transition is probably a disorder-induced Anderson localization; since the Bi substitution takes place within the conducting Ti$_2$Sb$_2$O layers. Besides, the increase of $c/a$ ratio reduces the dimensionality of the system, which may aggravate the disorder effect.

The detailed superconducting transitions in resistivity are displayed in figure 3. The parent compound shows a superconducting transition at $T^{onset}_{c}=1.5$ K, basically consistent with the previous report. With the Bi doping, $T_c$ first increases steadily up to 3.7 K at $x=0.17$, then decreases gradually for $x \geq 0.2$. A sharp superconducting transition at 0.8 K was still seen for the highest-doping sample with $x=0.40$. Note that an obvious resistivity drop always appears at 5.7 K for the high-doping samples. These samples contain remarkable impurity of bismuth (about 5% estimated from the relative intensities of the XRD peaks). This impurity could become superconducting owing to the quenching-like process during the sample preparations.

Figure 4 shows temperature dependence of magnetic susceptibility [$\chi(T)$] for the BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O samples down to the lowest temperature available ($\sim 2$ K). The magnetic susceptibility under $H=10$ kOe indicates the DW anomaly (marked by arrows) below 55 K for the low-doping samples. The anomaly is weakened and, $T_{DW}$ decreases rapidly with the Bi doping. No such anomaly can be detected for $x \geq 0.17$. These results are consistent with the above resistivity measurements shown in figure 2.

The superconducting diamagnetic transitions are also evident in the temperature scope. For $x=0.04$ and 0.08,
samples with lower $T_c$, only superconducting onset transitions can be seen [the inset of Fig. 4(d)]. The transition temperature determined by the magnetic measurement ($T_c^{\text{max}}$) agrees with the above resistivity measurement. Note that the diamagnetic transition at 5.7 K for the high-doping samples is again due to the superconducting transition from the Bi impurity. The $\chi(T)$ data in the ZFC mode show magnetic shielding fraction over 200% (because the theoretical density in the range of 6.0-6.7 g cm$^{-3}$ was employed, and no demagnetization correction was made) for the samples with higher $T_c$. The magnetic shielding signal is remarkably stronger than those of the parent compound$^{16}$ and Na-doped BaTi$_2$Sb$_2$O$^{17}$. In contrast, much lower diamagnetic signal (less than 1%) was measured in the FC mode. The vanishingly small magnetic repulsion suggests strong magnetic-flux trapping, which may be related to the Bi/Sb substitution disorder that could serve as a flux-pinning center.

Based on the above results, the electronic and superconducting phase diagram can be established in figure 5. The parent compound BaTi$_2$Sb$_2$O undergoes both a DW ordering at 55 K and a superconducting transition at 1.5 K. The DW state is suppressed by the Bi doping, and it disappears for $x \geq 0.1$. Meanwhile the superconducting transition temperature is elevated to its maximum value $T_c=3.7$ K at $x=0.17$. A M-NM transition locates at $x \sim 0.3$. Nevertheless, SC does not vanish at the nonmetal side, indicating that the SC is robust to disorder.

Very recently, Yajima et al.$^{23}$ succeeded in synthesizing the oxybismide end member BaTi$_2$Bi$_2$O, and an enhanced $T_c$ of 4.6 K with no DW anomaly was reported. This result is consistent with the case of lower doping ($x \leq 0.17$) BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O, which can be understood in terms of the lattice expansion/distortion associated with negative chemical pressure (see below). For the higher doping ($x \geq 0.2$) scenario, disorder effect induces Anderson localization and suppresses $T_c$. Therefore, for the Bi-rich ($0.5 < x < 1$) regime, we anticipate that $T_c$ would decrease monotonically if Bi is partially substituted by Sb in BaTi$_2$Bi$_2$O.

Therefore, the Bi doping in the 1221 system brings about two effects: lattice expansion and disorder. The former can be viewed as a consequence of negative pressure, which also leads to structural distortion of Ti$_2$Sb$_2$O-layers. The structural distortion of Ti$_2$Sb$_2$O-layers, measured by the $c/a$ ratio, is closely related to the DW state and possibly to SC also. The negative chemical pressure increases the $c/a$ ratio, hence decreases $T_{\text{DW}}$ and correspondingly increases $T_c$. However, the maximum $T_c$ is still about 1 K and 2 K lower than those of BaTi$_2$Bi$_2$O$^{24}$ and the Na-doped BaTi$_2$Sb$_2$O$^{17}$. This implies that the Bi/Sb substitution disorder plays a role. In the high-doping region, such disorder leads to an Anderson localization that is responsible for the observed M-NM transition. Surprisingly, SC still appears when the normal state shows nonmetallic behaviors (negative TCR and relatively high resistivity). This fact suggests a possible realization of “fractal superconductivity” near the localization threshold in the present system.$^{26}$ This interesting issue deserves future explorations.

In summary, we have investigated an isovalent substitution effect on SC and CDW/SDW in BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O system. The Bi doping induces negative chemical pressure which not only expands but also distorts the lattice. It was found that the CDW/SDW ordering was completely suppressed at $x=0.17$, and concomitantly the superconducting transition temperature was elevated to the maximum $T_c$ of 3.7 K. A metal-to-nonmetal transition at $x \sim 0.3$ was observed, which is interpreted by Anderson localization due to the Bi/Sb substitution disorder. Interestingly, such disorder does not kill the superconductivity. These results supply some useful clues to further study the nature of the CDW/SDW phase and its relations to superconductivity in BaTi$_2$Sb$_2$O-related systems.
FIG. 5: (Color online) Electronic and superconducting phase diagram of BaTi$_2$(Sb$_{1-x}$Bi$_x$)$_2$O. DW refers to spin- or charge-density wave state. The phase boundaries are determined by both resistivity ($T^{\text{res}}$) and magnetic susceptibility ($T^{\text{mag}}$) measurements. Note that the vertical axis was broken from 5 to 20 K in order to show the related phases clearly.

Acknowledgments

This work is supported by the NSF of China (No. 11190023), the National Basic Research Program of China (Nos. 2010CB923003 and 2011CBA00103), and the Fundamental Research Funds for the Central Universities of China.

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