Growth and characterizations of Ba₂Ti₂Fe₂As₄O single crystals

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Abstract
Single crystals of a new iron-based superconductor Ba₂Ti₂Fe₂As₄O have been grown successfully via a Ba₂As₃-flux method in a sealed evacuated quartz tube. Bulk superconductivity with Tc ∼ 21.5 K was demonstrated in resistivity and magnetic susceptibility measurements after the as-grown crystals were annealed at 500 °C in vacuum for a week. X-ray diffraction patterns confirm that the annealed and the as-grown crystals possess the identical crystallographic structure of Ba₂Ti₂Fe₂As₄O. Energy-dispersive x-ray spectra indicate that partial Ti/Fe substitution exists in the [Fe₂As₂] layers and the annealing process redistributes the Ti within the Fe-plane. The ordered Fe-plane stabilized by annealing exhibits superconductivity with magnetic vortex pinned by Ti.

Keywords: Ba₂Ti₂Fe₂As₄O, iron-based superconductor, single crystal growth

1. Introduction
Since high-temperature superconductivity was reported in iron pnictides in 2008 [1], great efforts have been made to explore new iron-based superconductors. So far, several crystallographic types of iron-based superconductors have been discovered. They include REFeAsO (RE = rare earth, ‘1111’) [1], AFeAs (A = Li, Na or K, ‘111’)[2], AEFexAsy (AE = Ca, Sr, Ba or Eu, ‘122’) [3, 4] and FeX (X = Se or Te, ‘11’)[5] systems. Among them, the ‘122’ system has attracted the most interest because it yields sizable single crystals [6–9], which makes it possible to investigate intrinsic physical properties and to understand the superconducting mechanism of iron-based superconductors.

Recently, our group designed and successfully synthesized a new iron-based superconductor Ba₂Ti₂Fe₂As₄O with Tc ∼ 21.5 K [10]. This compound contains not only the same [Fe₂As₂] layer as in other iron-based superconductors, but also another conducting sheet [Ti₂O], which makes it very distinctive. First-principles studies suggest that the intercalated [Ti₂O] layers, with a possible charge/spin-density wave (CDW/SDW) ordering, transfer 0.12e charge to the [Fe₂As₂] layers, which causes superconductivity in the [Fe₂As₂] layers without explicit doping [11]. Later, a series of compounds with superconductivity originating from the [Ti₂O] sheets were reported [12–14]. So, the coupling between the [Fe₂As₂] layers and the [Ti₂O] sheets in Ba₂Ti₂Fe₂As₄O, both being possibly superconducting, is an intriguing issue. This calls for more experimental studies of the intrinsic physical properties, which requires the growth of Ba₂Ti₂Fe₂As₄O single crystals.

An FeAs-flux method [7–9] is efficient for growing oxygen-free crystals, such as those of the ‘122’ system, but not for oxypnictides such as Ba₂Ti₂Fe₂AsO₃. Recently, by employing a NaAs-flux method, the ‘1111’ oxypnictides were successfully grown [15, 16]. To avoid introducing extra elements, Ba₂As₃ was chosen as the flux for growing Ba₂Ti₂Fe₂As₄O single crystals, since it has been used to grow sizable single crystals of doped BaFe₂As₂ [17]. In this paper, we report a successful trial to grow Ba₂Ti₂Fe₂As₄O single crystals. By annealing the crystals for a week, we obtained crystals with bulk superconductivity at 21.5 K. The as-grown...
and annealed crystals were both studied through x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS) analysis, and we conclude that superconductivity is influenced by the level of Ti/Fe substitution in [Fe$_2$As$_2$] layers.

2. Experimental details

The flux, with nominal compositions of Ba$_2$As$_3$, was prepared by reacting Ba and As (Alfa Aesar, $\geq$99.9%) in a sealed quartz tube, which was then heated to 700 °C at a rate of 30 °C h$^{-1}$ and held for 10 h. This precursor was mixed with some other starting materials (Alfa Aesar) at a molar ratio of TiO$_2$ ($\geq$99.9%):Ti (dehydrided, $\geq$ 99.9%):Fe ($\geq$99.5%):Ba$_2$As$_3$ = 1:3:4:6, pressed into a pellet and placed in an alumina crucible sealed in an evacuated quartz tube. All the operations were carried out in a glove box with the water and oxygen contents being less than 0.1 ppm. The mixture was heated to 1150 °C at the rate of 40 °C h$^{-1}$ and held for 10 h, then slowly cooled down to 900 °C at the rate of 2.5 °C h$^{-1}$. The flux was washed by dipping the as-prepared crystals in alcohol. Eventually, shiny plate-like crystals were harvested. In order to improve superconductivity, these as-grown crystals were annealed for another week at 500 °C in vacuum.

The quality of single crystals was checked by transmission Laue photography using a divergent white x-ray beam, and XRD using a PANalytical diffractometer (Empyrean Series 2) with Cu K$_\alpha$ radiation. The micrographs of single crystals were recorded with a field-emission scanning electron microscope (SEM), and the compositions were confirmed by EDS analysis. Electrical resistivity was measured by a standard four-terminal method using gold wires and silver paste. 2400 Digital Sourcemeter and 2182 Nanovoltmeter (Keithley Instruments) were employed, and the sample was cooled to 3 K in a helium-cycled refrigerator. Magnetic properties were measured on a Quantum Design Magnetic Property Measurement System (MPMS-5).

3. Results and discussion

The crystal structure of Ba$_2$Ti$_2$Fe$_2$As$_4$O is an intergrowth of BaFe$_2$As$_2$ and BaTi$_2$As$_2$O [10]. As shown in the inset of figure 1, blocks of Fe$_2$As$_2$, Ba and Ti$_2$As$_2$O are stacked along the c-axis of the tetragonal cell, which makes this layered crystal structure belong to I4/mmm space group. The phase purity was examined by XRD with powder obtained by crushing the single crystals, and the XRD patterns are shown in figure 1. One can see that the XRD patterns can be well indexed with a tetragonal unit cell and only the peaks for Miller index ($h k l$) with $h + k + l = 2n$ (here $n$ stands for a natural number) are observed. These results coincide with the structural model as shown in the inset of figure 1. The detailed lattice parameters were then calculated to be $a$-axis of 4.033 Å and $c$-axis of 27.38 Å, consistent with our previous report [10].

These single crystals, with plate-like morphology, are easily cleaved along the $ab$ planes. Figures 2(a) and (b) show the X-ray rocking curve and full-width at half-maximum for (0016) reflection of the annealed crystals. The inset of (c) is the x-ray transmission Laue photograph of Ba$_2$Ti$_2$Fe$_2$As$_4$O single crystal in the x-ray perpendicular to the $ab$-plane.
show the XRD patterns of as-grown and annealed crystals, respectively. Sharp peaks of (00I) reflections were observed in both profiles and lattice parameters of single crystals stay unchanged before and after annealing, which suggests that the crystals are of high quality and the annealed crystals keep the same crystallographic structure. In addition, the FWHM (Δθ) of Ba2Ti2Fe2As4O single crystal (001θ) rocking curve (θ scan, shown in figure 2(c)) was as small as 0.06°, indicating that these crystals are of high quality. The inset of figure 2(c) is the x-ray transmission Laue photograph of Ba2Ti2Fe2As4O single crystal in the x-ray beam perpendicular to the ab-plane. The fourfold symmetry in the Laue photograph confirms the tetragonal structure of Ba2Ti2Fe2As4O crystals. Insets of figures 2(a) and (b) are photographs of Ba2Ti2Fe2As4O single crystals placed on millimeter grids, whose typical sizes are 4 x 3 x 0.2 mm3. As shown, the as-grown crystals are bright, while the annealed crystals are dim, consistent with the fact that tiny impurities separated out on the surface (see figure 3(b)). In figure 2(b), one can see a very tiny extra peak around 2θ ~ 45.3° (marked with “z”), which is possibly the (110) reflection of Fe2Ti2O. This might be some kind of surface contamination due to oxygenation in the annealing process.

SEM micrographs are shown in the upper panels in figure 3. The surface of as-grown crystals is much more smooth than that of annealed crystals, which meets the fact that there is tiny impurity on the surface of annealed crystals. EDS data were collected on the region framed with pink line, and the typical spectra are shown in the lower panels of figure 3. Compositions of as-grown and annealed crystals are listed in table 1 (oxygen content is not displayed because it cannot be accurately determined by EDS).

As displayed in the table, the ratio of Ba:Ti:Fe:As is nearly 2:2:2:4 for both specimen, confirming the Ba2Ti2Fe2As4O phase. However, the Ti content is distinctly higher than the Fe content, indicating Ti/Fe substitution in the [Fe2As2] layers. In annealed crystals, the Ti content seems to decrease, which is possibly related to the impurity separated out.

Figure 4 shows the electrical resistivity in the ab-plane of as-grown and annealed crystals. As shown, only traces of superconductivity appear in as-grown crystals while for annealed crystals, superconducting transition occurs at Tc onset ~ 21.5 K with zero resistance at Tc zero ~ 17 K. According to the EDS and XRD analyses, the Ti/Fe substitution in the [Fe2As2] layers destroys the integrity of the Fe-plane and suppresses superconductivity. The appearance of superconductivity can be explained in terms of annealing-stabilized complete Fe-plane. It is in the Fe-plane with little occupancy of Ti that superconductivity occurs. However, in comparison with polycrystalline sample [10], normal-state resistivity of the as-grown crystals shows a semiconductor-like behavior at low temperatures, indicating that there is still some Ti occupying in the Fe-plane, which may serve as magnetic vortex pinning centers (see discussions on figure 5). Note that the resistivity upturn at Tc ~ 125 K, associated with a CDW/SDW transition in the [Ti2O] sheets, remains unchanged. It means that annealing has no influence on CDW/SDW ordering in the [Ti2O] sheets.

Magnetic properties of these superconducting crystals were then measured on MPMS with the applied field parallel to the c-axis and the ab-plane, respectively. Figure 5 shows temperature dependence of magnetic susceptibility in ZFC and FC modes under H = 1 Oe. Both ZFC and FC curves for the two field orientations (c-axis and ab-plane) drop around 21.5 K, which corresponds with the superconducting transition in the resistivity measurement. The magnetic shielding volume fraction ~ 90% defined by 4πχ (ZFC) and magnetic expelling fraction only ~ 4.1% by 4πχ (FC) with field applied along the c-axis at 2 K indicate that this compound is a bulk superconductor with flux pinning. This phenomenon is very common in doped iron-based
The annealing process redistributes the occupancy of Ti within the Fe-plane, which leads to the appearance of superconductivity in [Fe₂As₂] layers. Another feature of the superconductor is that it contains [Ti₃O] sheets which undergo a CDW/SDW transition at 125 K. With such special characteristics, the single crystals of Ba₂Ti₃Fe₂As₄O deserve future in-depth investigations by transport measurements and optical and angle-resolved photoemission spectroscopies.

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