Enhanced Superconductivity in Rock-Salt TiO

Dong Wang, ‡,§ Chong Huang, ‡,§ Jianqiao He, ‡ Xiangli Che, ‡ Hui Zhang, ‡ and Fuqiang Huang ‡,#

‡ State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China
§ State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

ABSTRACT: Oxygen stoichiometry is critical for physical properties, but it is hard to precisely control in many multivalent transition metal oxides, for example, cuprate superconductors, magnetoresistive manganite oxides, and TiO$_x$ ($x<2$). We have developed a new method to synthesize rock-salt TiO in a sealed and evacuated quartz tube by using KClO$_4$ as the only oxygen source to react with elemental Ti (in a Ti/O molar ratio of 1:1). The stoichiometric titanium monoxide (TiO) exhibits an enhanced superconductivity transition temperature ($T_c$) of 5.5 K, which is superior to the reported results of 0.5–2.3 K. The new synthetic method provides an excellent way to prepare stoichiometric oxides, and the enhanced superconductivity of TiO may initialize the restudy of the transport properties of Ti-containing oxides.

1. INTRODUCTION

Oxygen vacancies and oxygen content are hard to precisely control in the preparation of many multivalent transition metal oxides, but they are extremely critical for their physical properties. For example, the superconductivity transition temperature ($T_c$) in cuprates depends on the oxygen stoichiometry, which is related to the oxidation states of Cu.$^{1,−3}$ and the colossal magnetoresistance properties depend on the oxidation state of Mn in manganite oxides.$^{4,−6}$ Similarly, Fe stoichiometry in the Sr$_2$FeMoO$_6$ system affects the magnetoresistive properties significantly.$^{7,8}$ However, the traditional solid-state chemistry method for preparing oxides is to place the starting materials into a muffle furnace, and then the products are automatically obtained with an un-tunable oxygen content. Sometimes, the gas flow, as a specific reaction atmosphere, is used to adjust the oxidation state of the transition metal or oxygen vacancies.$^{9,10}$ Until now, few methods reported have been able to accurately control the oxygen stoichiometry in the many multivalent transition metal oxides mentioned above, as well as that in subvalent titanate.

The superconductivity in titanate-related compounds started to attract enormous attention due to the interfacial superconductor between two insulating dielectric layers of the perovskite oxides LaAlO$_3$ and SrTiO$_3$.$^{11−14}$ The source of the charge carriers in this superconductor system appealed to many researchers.$^{11,12,14}$ One possible source of charge carriers might be produced in a polar catastrophe, which is related to the TiO$_2$-terminated layer of SrTiO$_3$.$^{15}$ Similarly, a higher superconductivity transition temperature up to 65 K was observed in a single-layer FeSe thin film grown on a (001) TiO$_2$-terminated SrTiO$_3$ substrate.$^{16−19}$ compared to that of the bulk FeSe ($T_c = 8$ K).$^{20}$ More surprisingly, the $T_c$ was reported to be as high as 109 K.$^{21}$ Structurally, the exposed Se atoms of single-layer FeSe strongly interact with the Ti atoms in the TiO$_2$-terminated layer. How the terminated-TiO$_2$ layer plays an indispensable role in increasing $T_c$ is unclear. The oxygen vacancies in the terminated-TiO$_2$ layer have been frequently discussed and many structural models have been proposed.$^{22,23}$ The terminated-TiO$_2$ layer on the surface of SrTiO$_3$ can be considered as a layer which was extracted from bulk titanium monoxide (TiO). Recently, Li’s group$^{24}$ fabricated an epitaxial thin TiO film on Al$_2$O$_3$ ((0001) orientation), and an enhanced superconductivity transition at 7.4 K was obtained. However, the physical properties of TiO are also not very clear. Thus, it is significant to investigate bulk TiO in diverse ways to figure out its unique transport properties so as to contribute to the understanding of the interface superconductivities of multilayer LaAlO$_3$/SrTiO$_3$, FeSe/SrTiO$_3$, and FeSe/TiO.

Titanium monoxide (TiO) has four different phases: (1) cubic TiO with a rock-salt structure (a = 4.174 Å)$^{25,26}$ (2) β-TiO with a superstructure of rock-salt TiO (a = 12.54 Å)$^{27}$ (3) monoclinic α-TiO (a = 5.860 Å, b = 9.340 Å, c = 4.141 Å, γ = 107.553°)$^{28−30}$ and (4) hexagonal e-TiO (a = 4.9936 Å, c = 2.8773 Å).$^{31}$ The rock-salt TiO phase is composed of a nonstoichiometric compound with a wide composition range from TiO$_{0.7}$ to TiO$_{1.25}$. There is a large amount of vacancies, even in crystal lattices.$^{32−37}$ Therefore, it is very difficult to synthesize relatively pure rock-salt TiO samples. Here, we develop a new solid-state chemistry method to prepare rock-salt TiO samples at 1273 K in a sealed and evacuated quartz tube, by using KClO$_4$ and elemental Ti powder as the raw materials (in a molar ratio of 1:1). High-purity KClO$_4$ powder is used as...
the reactant to precisely provide the oxygen content in TiO,
and KCl, produced from the decomposition of KClO₄, is used
as flux. The superconductivity transition temperature of the
rock-salt TiO sample was enhanced to 5.5 K, and was
compared with the reported results of 0.5–2.3 K.²⁹,³⁸,³⁹

2. RESULTS AND DISCUSSION

The powder X-ray diffraction (PXRD) pattern of the obtained
TiO is shown in Figure 1. The five main peaks of the TiO can
be well indexed with the simulated data, using Jade 6.5, based
on a cubic cell (space group: F432) with the cell parameter \(a =
4.228 \text{ Å}\), which reveals the main phase of the superconductivity
phase. The black bars are the Bragg positions of rock-salt TiO
with a NaCl-type structure (PDF: #89-3660), and the lattice
parameter \(a = 4.174 \text{ Å}\). The inset in Figure 1 shows the NaCl-
type crystal structure of the cubic TiO, where the red spheres
represent oxygen atoms and the pink spheres represent
titanium atoms. The ratio of O/Ti is 0.96 according to our
thermogravimetry results.

Figure 2a shows the temperature-dependent magnetic
susceptibility of the as-prepared TiO measured under an
applied magnetic field of 5 Oe. The black and red lines indicate
the zero-field cooling (ZFC) and field cooling (FC) curves,
respectively. The onset superconductivity transition temper-
\(a\)ture of as-prepared TiO is about 5.5 K. The superconductivity
volume fraction is estimated to be 88% from the ZFC magnetic
susceptibility at 2 K, indicating bulk superconductivity. Figure
2b depicts the isothermal magnetization versus applied
magnetic field curve at 2 K in applied fields up to 1 T. The
obvious magnetic hysteresis curve for a second class super-
conductor can be observed and confirms the superconductivity.
The left inset pattern in Figure 2b shows the lower magnetic

Figure 1. (a) XRD pattern of rock-salt TiO. The black bars represent
the Bragg positions of cubic TiO (PDF: #89-3660); the inset shows
the schematic crystal structure of cubic TiO (NaCl-type). (b) XRD
pattern of the magnified (111) peak of as-prepared TiO.

Figure 2. (a) Temperature dependence of the direct current magnetic susceptibility of cubic TiO measured under a magnetic field of 5 Oe in the
processes of ZFC and FC. (b) Magnetic hysteresis of the TiO measured at 2 K in magnetic fields up to 1 T; the left inset shows the lower critical
magnetic field. (c) Temperature dependence of the resistivity of cubic TiO, the inset shows the enlarged pattern of the resistivity transition. (d)
Electrical resistivity measured under the magnetic fields from 0 to 2 T; the right inset displays the temperature dependence of the upper critical field.
field, the $H_{c2} (2 \text{ K})$ can be estimated to be 180 Oe from the intercept of the tangent in the $H$ axis.

Figure 2c demonstrates the electrical resistivity as a function of temperature from 2 to 300 K at zero applied magnetic field. A clear resistivity transition can be observed. The resistivity decreased with temperature cooling down to 5.5 K and reached zero resistivity at 2.8 K. The onset superconductivity transition temperature is consistent with the $T_c$ derived from the temperature dependence of magnetic susceptibility shown in Figure 2a. The resistivity of cubic TiO in different magnetic fields from 0 to 2 T is shown in Figure 2d. The onset superconductivity transition temperature decreased gradually with increasing applied magnetic field from 0 to 2 T, which indicates the characteristic of a second class superconductor with a gradual destruction of the superconductivity state. With a higher applied magnetic field above 1.5 T, the transition point was not observed and the normal state appeared under this condition.

The upper critical magnetic field dependence of the superconductivity transition temperature is presented in the inset of Figure 2d. According to the Bardeen–Cooper–Schrieffer theory, the upper critical magnetic field $H_{c2}$ at 0 K is determined by the Werthamer–Helfand–Hohenberg formula $H_{c2} (0 \text{ K}) = 0.693\left[-(dH_{c2}/dT)\right]_T \cdot T_c$. Using $-dH_{c2}/dT|T = -1.56 \text{ TK}^{-1}$, $T_c = 5.5 \text{ K}$, the estimated $H_{c2} (0 \text{ K})$ is 8.58 T for the as-prepared TiO.

3. CONCLUSIONS

In conclusion, superconductivity-enhanced rock-salt TiO powder was prepared by a newly-developed method using KClO$_4$ as the reactant. The cell constant of the obtained cubic TiO with parameter $(a)$ was determined to be equal to 4.228 Å. The obtained rock-salt TiO is a type-II superconductor and the onset superconductivity transition temperature ($T_c$) is 5.5 K, which is higher than previously reported results.

4. EXPERIMENTAL SECTION

The phase-pure TiO was prepared by the solid-state method using stoichiometric Ti powder (99.99%, Aladdin) and KClO$_4$ (99.99%, Aladdin) as raw materials at 1273 K. For each typical preparation, 0.1160 g of Ti and 0.0840 g of KClO$_4$ powder were weighed in a Ti/O molar ratio of 1:1 to synthesize the TiO compound, and the total weight of the Ti powder and KClO$_4$ powder was maintained at 0.2 g. The mixture was placed into a quartz tube and the tube was flame-sealed under a vacuum of less than 10$^{-3}$ bar. Due to the decomposition of KClO$_4$ at 673 K and the silica tube only being able to stand up to 0.2 MPa gas pressure, the silica tube must be heated to reaction temperature over enough time. Subsequently, the tube was heated to 1273 K in 15 h then kept at 1273 K for 24 h in a programmable furnace, and finally, the tube was quenched into cold water to harvest the rock-salt TiO phase. PXRD data were collected on a Bruker D8 Focus X-ray diffractometer using Cu Kα radiation at room temperature. The magnetic properties were measured using a Superconductivity Quantum Interference Device (SQUID) magnetometer with a magnetic field of 5 Oe in the processes of ZFC and FC, and the resistivity measurements within 2–300 K were performed using the standard four-probe method on a Quantum Design Physical Property Measurement System (PPMS). The thermogravimetric measurements were taken in a Thermal Analysis Mass Spectrometer (STA449C).
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