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Bulk Superconductivity in Bismuth Oxysulfide $Bi_4O_4S_3$

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ABSTRACT: A very recent report on the observation of superconductivity in $Bi_4O_4S_3$ [Mizuguchi, Y.; et al. http://arxiv.org/abs/1207.3145] could potentially reignite the search for superconductivity in a broad range of layered sulfides. We report here the synthesis of $Bi_4O_4S_3$ at 500 °C by a vacuum encapsulation technique and its basic characterizations. The as-synthesized $Bi_4O_4S_3$ was contaminated with small amounts of Bi_2S_3 and Bi impurities. The majority phase was found to be tetragonal (space group *I*4/*mmm*) with lattice parameters $a = 3.9697(2)$ Å and $c = 41.3520(1)$ Å. Both AC and DC magnetization measurements confirmed that $Bi_4O_4S_3$ is a bulk superconductor with a superconducting transition temperature (T_c) of 4.4 K. Isothermal magnetization ($M-H$) measurements indicated closed loops with clear signatures of flux pinning and irreversible behavior. The lower critical field (H_{c1}) at 2 K for the new superconductor was found to be ~15 Oe. Magnetotransport measurements showed a broadening of the resistivity (ρ) and a decrease in T_c ($\rho = 0$) with increasing magnetic field. The extrapolated upper critical field $H_{c2}(0)$ was ~31 kOe with a corresponding Ginzburg–Landau coherence length of ~100 Å . In the normal state, the $\rho \sim T^2$ dependence was not indicated. Hall resistivity data showed a nonlinear magnetic field dependence. Our magnetization and electrical transport measurements substantiate the appearance of bulk superconductivity in as-synthesized $Bi_4O_4S_3$. On the other hand, Bi heat-treated at the same temperature is not superconducting, thus excluding the possibility of impurity-driven superconductivity in the newly discovered superconductor $Bi_4O_4S_3$.

The discovery of superconductivity at 26 K in $LaO_{1-x}F_xFeAs$[1] has ignited a gold rush in the search for new superconductors. Besides popular Fe-based pnictides[1,2] and chalcogenides,[3] some new interesting systems have also appeared, including $CeNi_{0.8}Bi_2$,[4] BiOCuS,[5] and doped $LaCo_2B_2$.[6] The superconducting transition temperatures (T_c) for these systems are ~4 K. These compounds are layered with relatively large unit cells and mimic the superconducting characteristics of CuO_2-based high-T_c cuprates and FeAs-based pnictides. A comprehensive theoretical understanding of the mechanisms of CuO_2- and FeAs-based high-T_c superconductivity is still awaited. The hybridization of Cu–O and Fe–As in these strongly correlated systems along with their multiband character has been of prime interest to the scientific community.[7,8] After the recent observations of superconductivity in BiOCuS[5] and doped $LaCo_2B_2$,[6] it is pertinent to ask whether CuS and CoB could also play the same role as CuO_2 and FeAs. In this regard, it is worth mentioning that although the superconductivity of BiOCuS could not be reproduced,[9] the $CeNi_{0.8}Bi_2$ and doped $LaCo_2B_2$ still lack independent confirmation. For example, the volume fraction of superconductivity in $CeNi_{0.8}Bi_2$ is very small.[10] In this sense, the observation of superconductivity at ~4 K in $Bi_4O_4S_3$[11] has once again started the debate over whether the superconductivity of this newest series of materials is intrinsic. It has been suggested that the superconductivity of $Bi_4O_4S_3$ is BiS_2-based and that the doping mechanism is similar to that of cuprates and pnictides.[12,13] The central question is whether the observed superconductivity in $Bi_4O_4S_3$ is intrinsic or triggered by Bi impurities in the matrix.

Bismuth has been a part of various superconducting compounds, such as Bi-based high-T_c cuprates,[14] Bi_3Ni,[15,16] and $CeNi_{0.8}Bi_2$.[4] On the other hand, pure Bi is found in several phases; ordinary rhombohedral Bi is non-superconducting,[17,18] while some other phases have been found to be superconducting.[19−23] Various crystallographic phases of pure Bi that are superconducting in the bulk phase are Bi-II, -III, and -V (high-pressure phases of Bi), for which T_c = 3.9, 7.2, and 8.5 K,[19−21] respectively. The face-centered-cubic (fcc) Bi phase and amorphous Bi are superconducting with T_c ~ 4[22] and 6 K,[23], respectively.

Here we report the extensive characterization of the newly discovered[11] superconductor $Bi_4O_4S_3$. The as-synthesized $Bi_4O_4S_3$ crystallized in a tetragonal structure with space group *I*4/*mmm*, and the main phase of the sample was contaminated with small impurities of Bi and Bi_2S_3. $Bi_4O_4S_3$ was found to be bulk-superconducting at ~4.4 K, as confirmed from magnetization and transport measurements. Interestingly, pure rhombohedral Bi heat-treated by the same route is non-superconducting. Thus, our results indicate that the superconductivity of $Bi_4O_4S_3$ is intrinsic and not driven by the Bi impurity phase.

$Bi_4O_4S_3$ was synthesized by a solid-state reaction route via vacuum encapsulation. High-purity Bi, Bi_2O_3, and S were weighed in the correct stoichiometric ratio and ground thoroughly in a glovebox under a high-purity argon atmosphere. The powders were subsequently pelletized and vacuum-sealed (10^{-4} Torr) in quartz tube. Sealed quartz ampule was placed in a box furnace, heat-treated at 500 °C for 18 h, and then cooled to room temperature naturally. The process was repeated twice.

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The synthesized $Bi_4O_4S_3$ sample was gray in color, in contrast to Bi, which is a shiny silver color. The X-ray diffraction (XRD) pattern of the compound was recorded on a Rigaku diffractometer. Rietveld refinement of the XRD pattern was carried out using FullProf software. The magnetization and transport measurements were carried out using 14 T Cryogenic Physical Property Measurement System (PPMS).

The Rietveld-refined room-temperature XRD patterns for the as-synthesized $Bi_4O_4S_3$ and a sample of Bi heat-treated at the same temperature are shown in Figure 1a. The $Bi_4O_4S_3$ sample crystallized in a tetragonal structure (space group $I4/mmm$). Rietveld refinement of the XRD patterns was carried out using the reported[11] Wyckoff positions. The positions and lattice parameters were further refined, giving lattice parameter values of $a = 3.9697(2)$ Å and $c = 41.3520(1)$ Å. The Wyckoff positions of the $Bi_4O_4S_3$ compound are given in Table 1. The heat-treated Bi sample cleanly crystallized in the rhombohedral phase. It can be concluded from the XRD results that the synthesized $Bi_4O_4S_3$ sample is nearly single-phase with some impurities of rhombohedral Bi and Bi_2S_3. Rhombohedral Bi has been reported to be non-superconducting.[17,18]

In previous work, the space group of the $Bi_4O_4S_3$ structure ($I4/mmm$ or $I\bar{4}2m$) was under debate.[11] The representative unit cell of the compound in the $I4/mmm$ space group is shown in Figure 1b. The layered structure includes Bi_2S_4 (rock salt-type), Bi_2O_2 (fluorite-type), and SO_4 layers. Superconductivity is induced in BiS_2 layer through hybridization of the Bi 6p and S 3p orbitals. Theoretical calculations[13] showed that bands are derived from Bi 6p and in-plane S 3p orbitals. These are the dominating bands for electron conduction and superconductivity.

Various atoms with their respective positions are labeled in Figure 1b, and their coordinates are provided in Table 1. Bi1, Bi2, Bi3, S1, and S2 occupy the 4e $(0, 0, z)$ site. The S3 atom is at the 2b $(0, 0, {}^{1}/_{2})$ site. O1 is situated at the 8g $(0, {}^{1}/_{2}, z)$ site, and O2 is positioned at the 16n $(0, y, z)$ site. The structural refinement indicated that the molecular composition is $Bi_3O_3S_{2.25}$, which is the $Bi_4O_4S_3$ composition normalized by ${}^{3}/_{4}$. The superconducting phase (i.e., $Bi_4O_4S_3$ or $Bi_3O_3S_{2.25}$) is 25% SO_4-deficient relative to the composition of the parent compound $Bi_3O_4S_{2.5}$ ($Bi_6O_8S_5$).[11]

The direct-current (DC) magnetization with temperature (M-T) of the $Bi_4O_4S_3$ sample is shown in Figure 2. The magnetization was measured using both the field-cooled (FC) and zero-field-cooled (ZFC) protocols under an applied magnetic field of 20 Oe. The compound shows a sharp onset of superconducting behavior at 4.4 K, which is clear from the zoomed inset in Figure 2. There is also evidence for substantial flux trapping. The bifurcation of the FC and ZFC data below T_c marks the irreversible region. From the ZFC diamagnetic susceptibility, the shielding fraction was determined to be ~95%. Both the FC and ZFC magnetization data confirmed the appearance of bulk superconductivity in $Bi_4O_4S_3$. To exclude a role of the Bi impurity in the superconductivity of $Bi_4O_4S_3$, we measured the magnetization of the Bi sample that was heat-treated at the same temperature (500 °C) and it is found to be non-superconducting (data not shown). It can be seen in Figure 1a that the heat-treated Bi sample crystallized in the non-superconducting[17,18] rhombohedral phase. This excludes the possibility that the superconductivity in $Bi_4O_4S_3$ is driven by unreacted Bi. In fact, the sufficient superconducting volume fraction and large shielding (~95%) of our studied sample discards the possibility that the superconductivity is driven by the minor impurity phase.

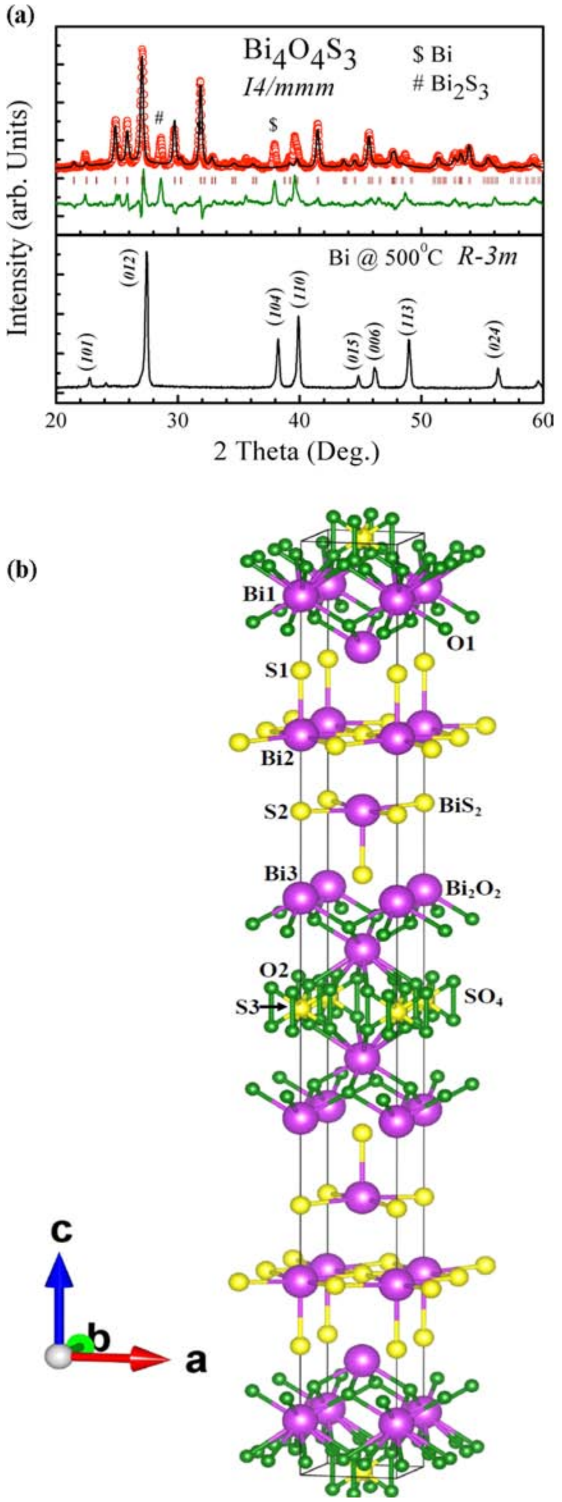

Figure 1. (a) Rietveld-refined room-temperature XRD patterns of as-synthesized $Bi_4O_4S_3$ and a sample of Bi heat-treated at the same temperature. (b) Schematic unit cell of the $Bi_4O_4S_3$ compound. Color code: Bi, violet; S, yellow; O, green.

The temperature dependence of the alternating-current (AC) susceptibility $\chi(T)$ of the $Bi_4O_4S_3$ sample is shown in Figure 3. The AC susceptibility was measured in an AC drive field with a frequency of 1 kHz and an amplitude of 10 Oe. The DC applied field was initially kept at zero to check the superconducting transition temperature and then increased to 5 and then 10 kOe

Table 1. Rietveld-Refined Wyckoff Positions and Fractional Occupancies of the Atoms in $Bi_4O_4S_3$

atom	x	y	z	site	fractional occupancy
Bi1	0.0000	0.0000	0.0583(4)	4e	1
Bi2	0.0000	0.0000	0.2074(2)	4e	1
Bi3	0.0000	0.0000	0.3821(2)	4e	1
S1	0.0000	0.0000	0.1383(1)	4e	1
S2	0.0000	0.0000	0.28901)	4e	1
S3	0.0000	0.0000	0.5000	2b	$^1/_2$
O1	0.0000	0.5000	0.0884(1)	8g	1
O2	0.0000	0.3053(1)	0.4793(2)	16n	$^1/_4$

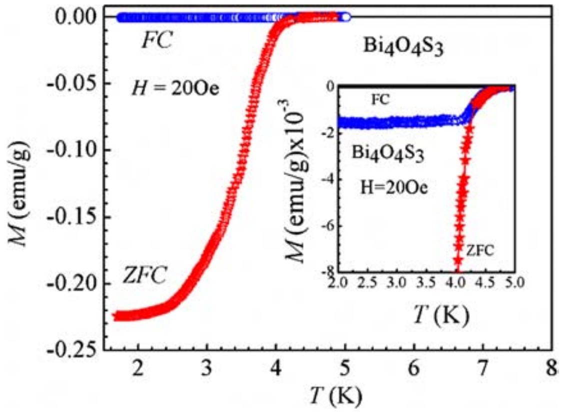

Figure 2. Temperature variation of the DC magnetization in the ZFC and FC modes for $Bi_4O_4S_3$ at 20 Oe. The onset T_c is identified at 4.4 K. The inset shows the expanded part of the same plot indicating irreversible behavior.

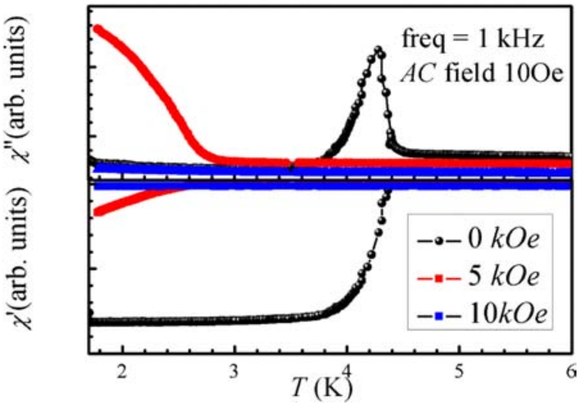

Figure 3. AC susceptibility $\chi(T)$ vs temperature for the $Bi_4O_4S_3$ sample at a frequency 1 kHz and an AC drive amplitude of 10 Oe under applied DC fields of 0, 5, and 10 kOe.

to check the AC losses in the mixed state. Both the real (χ') and imaginary (χ'') parts of the AC susceptibility were measured. χ' showed a sharp transition to diamagnetism at ~4.4 K, confirming the bulk superconductivity. On the other hand, χ'' exhibited a single, sharp, positive peak at around the same temperature. The presence of a single sharp peak in χ'' is indicative of better coupling of the superconducting grains in the studied $Bi_4O_4S_3$ superconductor. Under an applied DC field of 5 kOe, the χ' diamagnetic transition shifted to a lower temperature of 2.6 K, and the corresponding χ'' peak broadened and shifted to the same lower temperature. This is usual for a type-II superconductor. At a DC field of 10 kOe, neither χ' nor χ'' showed any transitions, indicative of rapid suppression of the superconductivity.

Figure 4 shows the isothermal magnetization versus magnetic field (M–H) curve for the sample at 2 K at applied fields of up to 3 kOe. The upper inset of the figure shows the same up to 1 kOe. The M–H curve in the lower inset shows that the initial flux penetration and the deviation from linearity marks the lower critical field (H_{c1}) of this compound as ~15 Oe at 2 K. The wide-open M–H loop of the studied $Bi_4O_4S_3$ compound demonstrates bulk superconductivity.

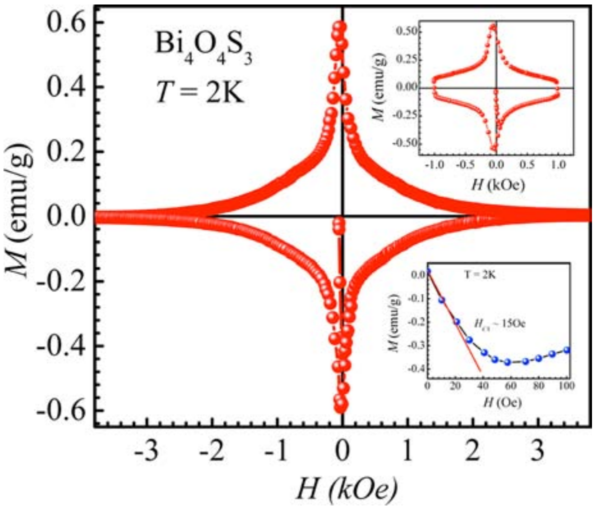

Figure 4. Isothermal magnetization vs magnetic field at 2 K in applied fields of up to 3 kOe. The insets show the same over smaller field ranges. H_{c1} at 2 K was estimated to be 15 Oe.

Figure 5 depicts the results of resistivity (ρ) versus temperature measurements with and without an applied magnetic field. The resistivity of the sample decreased with temperature and confirmed the onset of superconductivity at $T_c \approx 4.4$ K. The normal-state conduction (Figure 5 inset) is of the metallic type, and a T^2 fit was found to be inappropriate, implying non-Fermi liquid behavior. With applied fields of 1, 2, and 5 kOe,

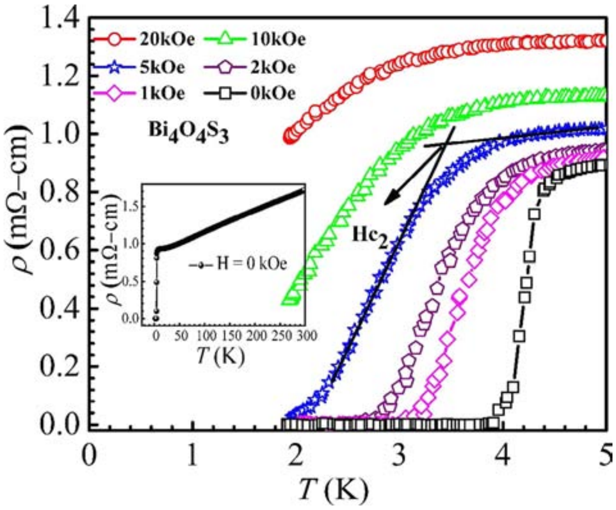

Figure 5. Resistivity vs temperature (ρ–T) behavior of $Bi_4O_4S_3$ in applied fields of 0, 1, 2, 5, 10, and 20 kOe in the superconducting region. The inset shows the zero-field ρ–T curve over the extended temperature range of 2–300 K.

T_c ($\rho = 0$) decreased to 3.2, 2.7, and 2 K, respectively. With even higher fields of 10 and 20 kOe, the T_c ($\rho = 0$) state was not reached, and only the onset T_c was seen. As sketched in Figure 5, we estimated the upper critical field $H_{c2}(T)$ using the conservative procedure of finding the intersection point of the lines from the linear regions of the normal-state resistivity and the superconducting transition line. While the applicability of the Werthamer–Helfand–Hohenberg (WHH) approximation can be debated in this new superconductor, a simplistic single-band extrapolation leads to a value of 31 kOe for $H_{c2}(0)$ [given by $-0.69T_c(dH_{c2}/dT)|_{T=T_c}$]. From this, the Ginzburg–Landau coherence length $\xi = [(2.07 \times 10^{-7})/(2\pi H_{c2})]^{1/2}$ was estimated to be ~100 Å.

A strong magnetoresistance in the normal state was also seen. It can possibly be ascribed to the Bi impurity in the matrix, similar to the effect of extra Mg impurity in MgB_2. Theoretical calculations predict that the superconducting in BiS_2 layers is of the multiband type.[13,24] In Figure 6, the Hall resistivity is plotted as a function of magnetic field at 10 K. The dominance of electronic charge carriers in the normal-state conduction mechanism is confirmed. Strong nonlinearity is observed with increasing magnetic field, which is suggestive of deviations from single-band analysis. The Hall coefficient R_H (Figure 6a inset) is field-dependent, and the carrier concentration at low field was estimated to be ~1.53×10^{19} cm^{-3} at 10 K, which increased to ~2.4×10^{19} cm^{-3} at 300 K.

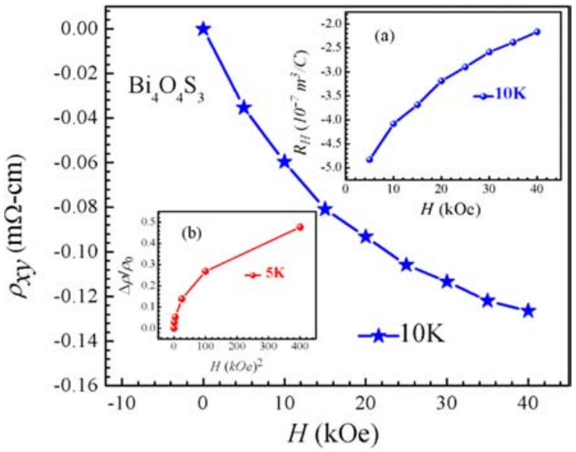

Figure 6. Hall resistivity as a function of magnetic field at $T = 10$ K. Insets: (a) variation of the Hall coefficient as a function of field; (b) normalized magnetoresistance at 5 K, implying a non-H^2 dependence.

Inset (b) of Figure 6 shows a plot of $\Delta\rho(H)/\rho(0)$ versus H^2 at 5 K for fields up to 20 kOe. One of the established features of multiband superconductivity is the H^2 dependence of $\Delta\rho(H)$ in the low-field range. Evidently, this dependence is not seen in this regime. We can conclude that while our Hall resistivity data may demand incorporation of more rigorous analysis, the magnetoresistance aspects in $Bi_4O_4S_3$ could be well due to the Bi impurity.

In conclusion, we have synthesized the new layered sulfide superconductor $Bi_4O_4S_3$ and established its bulk superconductivity by magnetization and transport measurements. Detailed Reitveld analysis determined the molecular composition to be $Bi_3O_3S_{2.25}$. The coherence length was estimated to be ~100 Å. A departure from strong electron–electron correlation in the normal state is indicated. The Hall resistivity yielded a nonlinear magnetic field dependence.

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Notes

The authors declare no competing financial interest.

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