



BiS₂-based layered superconductor Bi₄O₄S₃

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Exotic superconductivity has often been discovered in materials with a layered (two-dimensional) crystal structure. The low dimensionality can affect the electronic structure and can realize high transition temperatures (T_c) and/or unconventional superconductivity mechanisms. We show superconductivity in a new bismuth-oxysulfide compound Bi₄O₄S₃. Crystal structure analysis indicates that this superconductor has a layered structure composed of a stacking of spacer layers and BiS₂ layers. Band calculation suggests that the Fermi level for Bi₄O₄S₃ is just on the peak position of the partial density of states of the Bi 6*p* orbital within the BiS₂ layer. The BiS₂ layer will be a basic structure which provides another universality class for a layered superconducting family, and this opens up a new field in the physics and chemistry of low-dimensional superconductors.

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In the 100 years since the discovery of superconductivity, many superconductors have been discovered. In the early stages, new superconductors had been found in metallic compounds such as Nb-Ti alloy and Nb₃Sn. In 1986, Bednorz and Müller reported high- T_c superconductivity in (La,Ba)₂CuO₄ at 30 K.¹ After this discovery, a dramatic increase of T_c was achieved by optimizing the spacer layers and the number of CuO₂ planes, for example, in YBa₂Cu₃O_x ($T_c > 90$ K), Bi₂Sr₂Ca₂Cu₃O_x ($T_c > 110$ K) and HgBa₂Ca₂Cu₃O_x ($T_c > 130$ K).²⁻⁴ The high- T_c cuprates provided us with some strategies to explore new high- T_c superconductors, such as layered (low-dimensional) crystal structures, insulator-metal boundaries, electronic correlations, and the correlation between magnetism and superconductivity.

After the discovery of the cuprate family, some layered superconductors were discovered. Layered magnesium diboride MgB₂ exhibits a comparably high T_c of 39 K although it is a simple binary compound.⁵ Layered nitride HfNCl and ZrNCl are band insulators. However, when electrons are doped by intercalation of ions into the interlayer site, an insulator-metal transition occurs and a superconductivity of $T_c > 25$ K appears.^{6,7} As in the Hf-nitride superconductor, superconductivity in layered Co-oxide Na_xCoO₂ is induced by intercalation of H₃O⁺ ions into the interlayer site.⁸ Most recently, high- T_c superconductivity was discovered in Fe-based compounds. Kamihara and Hosono *et al.* reported that the antiferromagnetic metal LaFeAsO became superconducting ($T_c > 26$ K) when the O was partially substituted by F.⁹ Soon after the discovery, SmFeAsO_{1-x}F_x was reported to be a superconductor with $T_c > 55$ K.^{10,11} To date, more than 50 Fe-based superconductors with a layered structure, basically composed of superconducting layers of Fe-pnictogen (Fe₂As₂ or Fe₂P₂) or Fe-chalcogen (Fe₂Se₂ or Fe₂Te₂) layers and spacer layers, have been discovered.¹²⁻¹⁷ As introduced here, the discovery of a new layered superconductor provides us with a new research field in physics and chemistry. If a new superconducting layer is discovered, we will have a challenge for increasing T_c or exploring new superconductors

by changing the spacer layer or alignment of superconducting and spacer layers. We show superconductivity in a new layered superconductor bismuth-oxysulfide Bi₄O₄S₃, which is the first superconductor of the novel BiS₂-based superconducting family.

Polycrystalline samples of Bi₄O₄S₃ were prepared using a conventional solid state reaction method. All the chemicals were purchased from Kojundo Chemical Lab. At first, Bi₂S₃ was prepared by reacting Bi (99.99% grain) and S (99.9% grain) in an evacuated quartz tube above 500 °C. Starting materials of Bi₂S₃, Bi₂O₃ (99.9% powder), and S were ground, pelletized, sealed into an evacuated quartz tube, and heated at 510 °C for 10 h. The product was then well-ground, pelletized, and annealed at 510 °C for 10 h in an evacuated quartz tube. In the case that the Bi₄O₄S₃ sample was heated above 550 °C, S-O gas was produced. It should also be noted that heating the samples at high temperature may result in explosion of the quartz tube. Temperature dependence of magnetic susceptibility from 10 to 2 K after both zero-field cooling (ZFC) and field cooling (FC) was measured using a superconducting quantum interference device (SQUID) magnetometer with an applied magnetic field of 9.3 Oe. Temperature dependence of resistivity from 300 to 2 K was measured using the four terminal method. The T_c^{onset} was defined to be a temperature where the resistivity deviates from the linear extrapolation of normal-state resistivity as shown in the inset of Fig. 1(b). An x-ray-diffraction (XRD) pattern was collected by a RIGAKU x-ray diffractometer with Cu $K\alpha$ radiation using the 2θ - θ method. The diffraction peaks were indexed by the software X-CELL¹⁸ of Accelrys, Inc. The initial model of the crystal structure was derived from the software TOPAS of Bruker AXS, Inc. The structure was refined by the Rietveld-analysis program MATERIALS STUDIO REFLEX of Accelrys, Inc. Geometry optimizations were carried out using the density functional theory (DFT) methods with the program MATERIALS STUDIO CASTEP¹⁹ of Accelrys, Inc. The GGA (generalized gradient approximation)-PBEsol (Perdew-Burke-Ernzerhof for solids) exchange-correlation

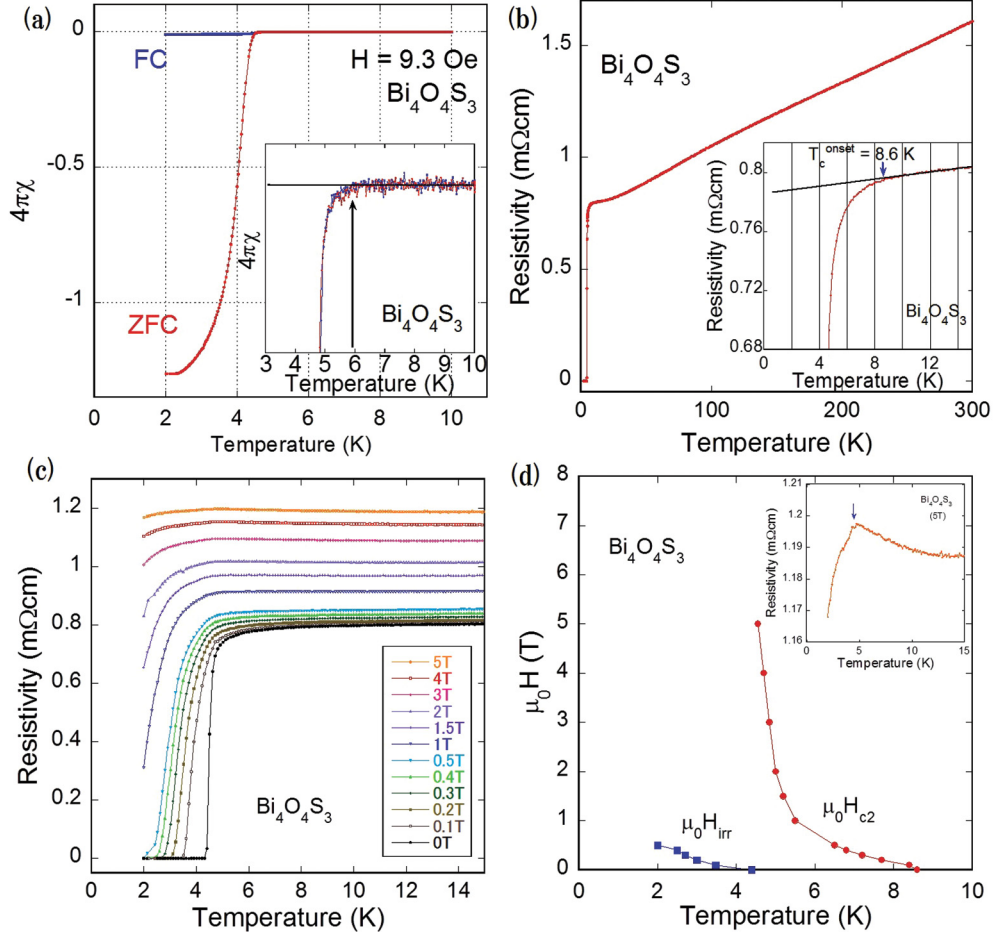


FIG. 1. (Color) Superconducting properties of $\text{Bi}_4\text{O}_4\text{S}_3$. (a) Temperature dependence of magnetic susceptibility for $\text{Bi}_4\text{O}_4\text{S}_3$. The inset shows an enlargement of onset of the superconducting (diamagnetic) signal. (b) Temperature dependence of resistivity for $\text{Bi}_4\text{O}_4\text{S}_3$. The inset is an enlargement of onset of the superconducting transition. (c) Temperature dependence of resistivity for $\text{Bi}_4\text{O}_4\text{S}_3$ under magnetic fields up to 5 T. (d) Magnetic field-temperature phase diagram in which the onset and zero-resistivity temperatures are plotted. The inset displays an enlarged superconducting transition of the temperature dependence of resistivity at 5 T.

functionals²⁰ and ultrasoft pseudopotentials²¹ were employed. The energy cutoff for the plane-wave basis set was 380.0 eV. The Monkhorst-Pack grid separation²² was set to $\sim 0.04 \text{ \AA}^{-1}$. The lattice parameters were set to the experimental values, and the atomic positions were optimized to minimize the total energy. The schematic images of the crystal structure were depicted using VESTA.²³ The band structure of $\text{Bi}_4\text{O}_4\text{S}_3$ shown in Fig. 3 was calculated using the WIEN2K package.²⁴ A GGA-PBESol exchange-correlation functional was adopted.²⁰ 512 k points and $RK_{\text{max}} = 7.0$ were taken. The spin-orbit interaction was omitted.

First, we show the physical properties of the new superconductor $\text{Bi}_4\text{O}_4\text{S}_3$. Figure 1(a) shows the temperature dependence of magnetic susceptibility (χ) for $\text{Bi}_4\text{O}_4\text{S}_3$ from 10 to 2 K. Both ZFC and FC data begin to decrease below 6 K as indicated by an arrow in the inset of Fig. 1(a). A large diamagnetic signal is observed below 4.5 K in the ZFC curve. The value of $4\pi\chi$ (ZFC) at 2 K exceeds -1 , indicating that the shielding volume fraction at 2 K is almost 100%. Namely, $\text{Bi}_4\text{O}_4\text{S}_3$ is a bulk superconductor. Figure 1(b) shows the temperature dependence of resistivity from 300 to 2 K for $\text{Bi}_4\text{O}_4\text{S}_3$. Resistivity linearly decreases with cooling and

begins to drop below ~ 8.6 K. An enlarged graph is displayed in the inset of Fig. 1(b). As indicated by an arrow in the inset, below 8.6 K, a decrease of resistivity—corresponding to the onset of superconducting transition—is clearly observed and resistivity reaches zero below 4.5 K. Temperature dependence of resistivity for $\text{Bi}_4\text{O}_4\text{S}_3$ under magnetic fields up to 5 T is displayed in Fig. 1(c). The superconducting states are destroyed by applying high magnetic fields. The increase of resistivity with applying magnetic fields could be due to the magnetic resistance of the impurity phase of the Bi. To investigate the temperature-magnetic field phase diagram for the superconductivity of $\text{Bi}_4\text{O}_4\text{S}_3$, we plotted T_c^{onset} and T_c^{zero} with the respective applied magnetic fields in Fig. 1(d). The T_c^{onset} at high magnetic fields was estimated as indicated by an arrow in the inset of Fig. 1(d). The T_c^{zero} linearly decreases with increasing magnetic field. By a linear extrapolation, the irreversible field $\mu_0 H_{\text{irr}}(0)$ is estimated to be ~ 1 T. The upper critical field $\mu_0 H_{c2}(0)$ was estimated to be ~ 21 T using the Werthamer-Helfand-Hohenberg theory,²⁵ which gives $\mu_0 H_{c2}(0) = -0.69 T_c (d\mu_0 H_{c2}/dT)|_{T_c}$, with a slope of T_c^{onset} for $H \geq 1.5$ T. In the inset of Fig. 1(d), we note that the temperature dependence of resistivity at high fields shows

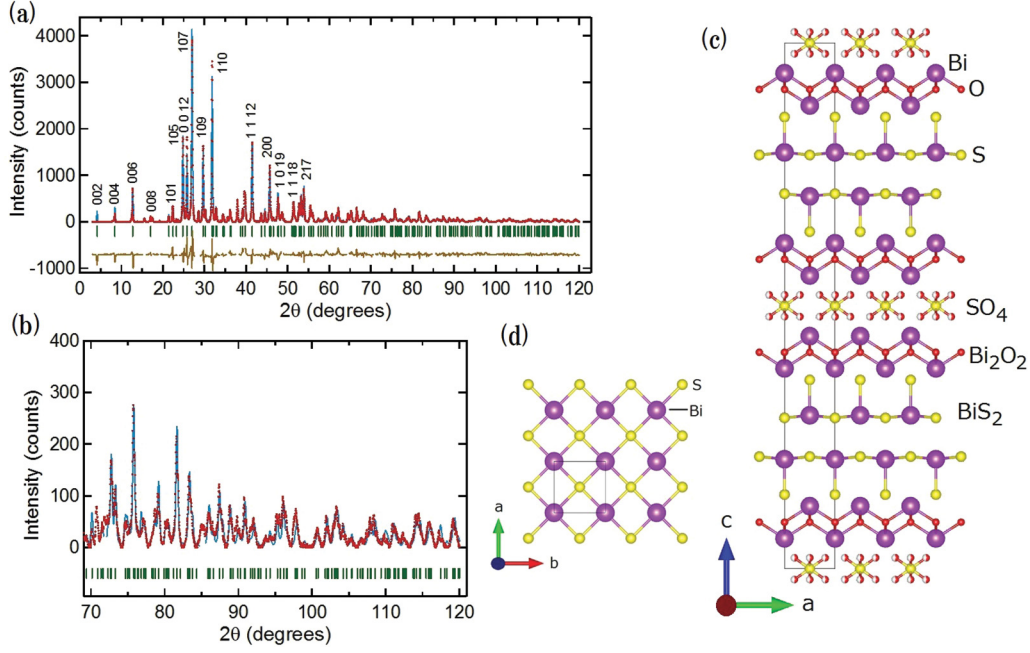


FIG. 2. (Color) Crystal structure analysis of new superconductor Bi₄O₄S₃. (a) XRD pattern with the result of the Rietveld refinement. The displayed numbers are the Miller indices. (b) XRD pattern at high angles. (c) Schematic image of the obtained crystal structure. Purple, yellow, and red circles indicate Bi, S, and O atoms, respectively. The occupancy of the O2 site (near $z = 0$ and 0.5) is 0.5 . The chemical composition can be described as Bi₆O₄S₄(SO₄)_{1-x} when defects of SO₄ ions exist. Bi₄O₄S₃ corresponds to $x = 0.5$ where the site occupancies of S3 and O2 in Table I are 0.5 and 0.25 , respectively. (d) Schematic image of the BiS₂ square lattice (ab plane).

a semiconducting-like behavior above T_c . This may indicate that superconductivity in Bi₄O₄S₃ occurs at the vicinity of insulating states. To summarize the physical properties of Bi₄O₄S₃, the T_c^{onset} and T_c^{zero} are 8.6 and 4.5 K at 0 T, respectively. The broadness of the transition is probably caused by an inhomogeneity of the local structure, carrier doping level, and/or the superconductivity nature close to the insulating state.

Next, we show the crystal structure obtained by Rietveld refinement of the powder XRD pattern and DFT calculations. At first, by indexing the observed peaks except for the small impurity peaks belonging to Bi₂S₃ and Bi, we obtained the I -centered tetragonal lattice with lattice parameters $a = 3.9592(1)$ and $c = 41.241(1)$ Å. The extinction rule suggested either $I4/mmm$ or $I-42m$ space groups as candidates. By fitting the XRD pattern with only Bi atoms at the Bi1, Bi2, and Bi3 sites in Table I, a reliability factor of $R_{\text{wp}} = 26.5\%$ was obtained. Furthermore, by adding S atoms at the S1, S2, and S3 sites in Table I to the refinement, an $R_{\text{wp}} = 16.0\%$ was achieved. Since both models for these space groups are completely identical, we selected the higher-symmetric $I4/mmm$. It is difficult to determine the O sites using only XRD data, therefore we performed structural optimization using DFT calculations. Additionally, we have confirmed the structural stability using molecular dynamics simulation. The atomic positions of Bi and S, determined by the XRD pattern, were only stable when the SO₄ ions occupied $z = 0$ and 0.5 . By using the structural model, we performed Rietveld refinement. Figure 2(a) shows the XRD pattern of this sample and the result of Rietveld refinement ($R_{\text{wp}} = 14.41\%$). The obtained atomic parameters and the site occupancy are summarized

in Table I. As shown in Fig. 2(b), the XRD pattern is well fitted at the high angle region. A schematic image of the final crystal structure is shown in Fig. 2(c). The layered structure is composed of Bi₂S₄ layers, Bi₂O₂ layers, and SO₄. The fluorite-type Bi₂O₂ layer is one of the well-known layers in the $I4/mmm$ or $P4/nmm$ tetragonal layered structures. In fact, Bi₂O₂SO₄ is a known compound. The rocksalt-type Bi₂S₄ layer structure has been found only in ROBiS₂ ($R = \text{Ce, Gd, and Dy}$) with the $P4/nmm$ space group.²⁶ Figure 2(d) is a schematic image of the Bi₂S₄ layer projected along the c axis. The Bi and S atoms form square lattices. The elemental composition of this crystal structure can be described as Bi₄O₄(SO₄)_{1-x}Bi₂S₄ where x indicates the occupancy of the SO₄ site. When all the sites are fully occupied, the atomic composition should be Bi₄O₄(SO₄)Bi₂S₄, namely, Bi₆O₈S₅. If the occupancy of the SO₄ site is 50% , the composition is Bi₄O₄S₃ corresponding to the superconducting composition.

TABLE I. Structural parameters of Bi₆O₄S₄(SO₄)_{1-x} ($x = 0$) obtained by Rietveld refinement.

Site	x	y	z	Occupancy
Bi1	0	0	0.0576(1)	1
Bi2	0	0	0.2082(1)	1
Bi3	0	0	0.3810(1)	1
S1	0	0	0.1410(3)	1
S2	0	0	0.2868(4)	1
S3	0	0	0.5	1
O1	0	0.5	0.0884 (fixed)	1
O2	0	0.3053 (fixed)	0.4793 (fixed)	0.5

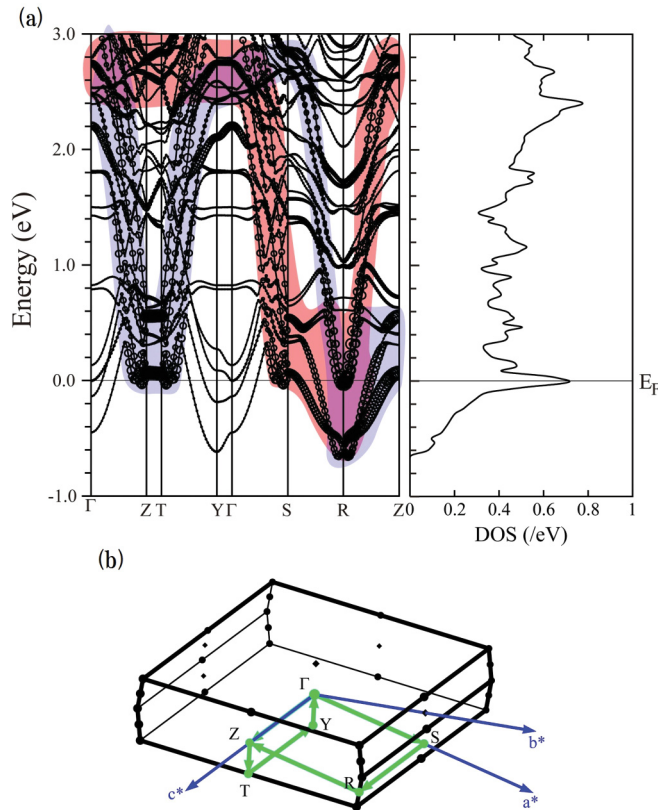


FIG. 3. (Color) Band structure and Brillouin zone of $\text{Bi}_4\text{O}_4\text{S}_3$. (a) Left panel: the band structure for $x = 0.5$. The radii of the circles represent the weight of the Bi $6p$ orbitals within the BiS_2 layer. The blue and red hatches indicate the bands having mainly p_x and p_y characters, respectively. Right panel: the partial density of states of the Bi $6p$ orbital within the BiS_2 layer. (b) The Brillouin zone is shown.

Therefore, we speculate that there are defects at the SO_4 site in our $\text{Bi}_4\text{O}_4\text{S}_3$ superconducting sample, because defects of molecules or ions at the interlayer site are often observed in layered compounds.

To discuss the nature of superconductivity in $\text{Bi}_4\text{O}_4\text{S}_3$, we performed band calculations for the parent and superconducting phases. It is found that $\text{Bi}_4\text{O}_4\text{S}_3$ ($x = 0.5$) is metallic, while $\text{Bi}_6\text{O}_8\text{S}_5$ ($x = 0$) is a band insulator with Bi^{3+} . In fact, the SO_4 deficiency generates electron carriers into the BiS_2 layers. Figure 3 shows the band structure for $x = 0.5$ ($\text{Bi}_4\text{O}_4\text{S}_3$) obtained using the WIEN2K package adopting the lattice structure obtained as above.²⁴ The Fermi level lies within the bands which mainly originate from the Bi $6p$ orbitals. In particular, the Fermi level is just on the peak position of the partial density of states of the Bi $6p$ orbital within the BiS_2 layer. Focusing on the contribution from the BiS_2 layer, it is found that the band structure near the Fermi level consists of p_x and p_y orbital contributions, which in itself has a quasi-one-dimensional nature, but mixes around the R point to result in a two-dimensional band structure. This quasi-one-dimensionality of the band structure should give good nesting at the Fermi surface, and this electronic feature may cooperate with the bosonic modes that mediate the pairing to enhance the pairing interaction. The enhanced

density of states at the Fermi level may also play a role in the Cooper pairing.

Finally, we compare the characteristics of $\text{Bi}_4\text{O}_4\text{S}_3$ with other layered superconductors. The crystal structure, composed of a stacking of the blocking and superconducting layers, resembles the cuprate and Fe-based superconductors. Furthermore, the fact that superconductivity occurs within the square-lattice sheets is a common feature. On the other hand, there are also some large differences in the electronic nature. The electronic bands that intersect the Fermi level of the cuprates and Fe-based superconductors originate mainly from the $3d$ orbitals, which have a localized nature. In the present BiS_2 -based system, the relevant bands originate from the $6p$ orbitals, which should have a less localized nature, and superconductivity takes place when electrons are doped into these bands. In this sense, it is interesting to compare them with HfNCl and ZrNCl , i.e., the layered nitride family, whose superconducting mechanism is still not understood and under debate. The relevant bands in these materials originate from $4d$ or $5d$ (less localized than $3d$) and $2p$ orbitals, and superconductivity occurs upon doping electrons in these bands.²⁷ In fact, the highest T_c is obtained at the vicinity of the insulator-metal transition in the nitride family, and this system has provided us with physics of low-carrier superconductivity.^{6,7} A very small electronic specific-heat coefficient has been observed in ZrNCl ,²⁸ and the relatively high T_c despite the low density of states has been puzzling in these materials. In fact, as a preliminary result, we have also observed very small electronic-specific-heat coefficients in the bulk superconducting $\text{Bi}_4\text{O}_4\text{S}_3$.²⁹ Therefore, the similarity between these two series of materials is quite intriguing. Although the pairing mechanism of $\text{Bi}_4\text{O}_4\text{S}_3$ is unclear at present, we believe that detailed studies on superconductivity in BiS_2 -based materials will provide new strategies to enhance T_c in layered superconducting materials.

In conclusion, we have discovered a new layered superconductor $\text{Bi}_4\text{O}_4\text{S}_3$. The crystal structure was found to be composed of the stacking of the superconducting BiS_2 layers and the blocking layers of $\text{Bi}_4\text{O}_4(\text{SO}_4)_{1-x}$. Band calculations indicated that the Fermi level for $\text{Bi}_4\text{O}_4\text{S}_3$ is just on the peak position of the partial density of states of the Bi $6p$ orbital within the BiS_2 layer. Finally, we introduce our latest report of the observation of superconductivity above 10 K in electron-doped LaOBiS_2 , which has a layered structure composed of a stacking of the BiS_2 superconducting layers and the La_2O_2 spacer layers.³⁰ This strongly suggests that the BiS_2 layer is a basic structure of a novel BiS_2 -based superconducting family, which will open up a new field in the physics and chemistry of low-dimensional superconductors, as have cuprates and Fe-based superconductors.

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