New layered fluorosulfide SrFBiS$_2$

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We have synthesized a new layered BiS$_2$-based compound SrFBiS$_2$. This compound has similar structure to BiS$_2$. It is built up by stacking up SrF layers and NaCl-type BiS$_2$ layers alternatively along the $c$ axis. Electric transport measurement indicates that SrFBiS$_2$ is a semiconductor. Thermal transport measurement shows that SrFBiS$_2$ has a small thermal conductivity and large Seebeck coefficient. First principle calculations are in agreement with experimental results and show that SrFBiS$_2$ is very similar to LaOBiS$_2$ which becomes superconductor with F doping. Therefore, SrFBiS$_2$ may be a parent compound of new superconductors.

I. INTRODUCTION

Low-dimensional superconductors with layered structure have been extensively studied and still attract much interest due to their exotic superconducting properties and mechanism when compared to conventional BCS superconductors. The examples include high $T_c$ cuprates Sr$_2$RuO$_4$, Na$_3$CoO$_2$H$_2$O, and iron-based superconductors. The discovery of LnOFepn (Ln = rare earth elements, Pn = P, As) in particular revitalises the study of layered compounds with mixed anions, paving a way to materials with novel physical properties. For example, Ln$_2$O$_2$TM$_2$OCh$_2$ (TM = transition metals, Ch = S, Se) show strong electron-electron interactions and Mott insulating state on the two dimensional (2D) frustrated antiferromagnetic (AFM) checkerboard spin-lattice. Very recently, bulk superconductivity was found in Bi$_2$-type layered compounds with mixed anions: Bi$_4$O$_4$S$_3$ and Ln(O,F)BiS$_2$. Experimental and theoretical studies indicate that these materials exhibit multiband behaviors with dominant electronic carriers originating from the Bi 6$p_x$ and 6$p_y$ bands in the normal state. On the other hand, compounds with mixed anions exhibit remarkable flexibility of structure. Different two-dimensional (2D) building blocks, such as [LnO]$^+$, [AEF]$^+$ (AE = Ca, Sr, Ba), [Ti$_2$OP$_n$]$^{2-}$, [FePn]$^-$, and [TM$_2$OCh$_2$]$^{2-}$, can sometimes be integrated to form new materials. Individual building blocks often keep their structural and electronic properties after being combined together.

In this work, we report the discovery of a new BiS$_2$-based layered compound SrFBiS$_2$. It contains NaCl-type BiS$_2$ layer and shows semiconducting behavior with relatively large thermopower. Theoretical calculation indicates that this compound is very similar to LnOBiS$_2$.

II. EXPERIMENT

A. Synthesis.

SrFBiS$_2$ polycrystals were synthesized by a two-step solids state reaction. First, Bi$_2$S$_3$ was prereacted by reacting Bi needles (purity 99.99%, Alfa Aesar) with sulfur flakes (purity 99.99%, Aldrich) in an evacuated quartz tube at 600 °C for 10 h. Then Bi$_2$S$_3$ was mixed with stoichiometric SrF$_2$ (purity 99%, Alfa Aesar) and SrS (purity 99.9%, Alfa Aesar) and intimately ground together using an agate pestle and mortar. The ground powder was pressed into 10 mm diameter pellets. We used a maximum pressure of 5 tons. The pressed pellet was loaded in an alumina crucible and then sealed in quartz tubes with Ar under the pressure of 0.15 atmosphere. The quartz tubes were heated up to 600 °C in 10 h and kept at 600 °C for another 10 h.

B. Structure and Composition Analysis.

Phase identity and purity were confirmed by powder X-ray diffraction carried out by a Rigaku Miniflex X-ray machine with Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). Structural refinement of powder SrFBiS$_2$ sample was carried out by using Rietica software. Synchrotron X-ray experiment was conducted at 300 K on X17A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The setup utilized X-ray beam 0.5 mm × 0.5 mm in size and $\lambda = 0.1839$ Å ($E = 67.4959$ keV), conditioned by two-axis focusing with one-bounce sagittally-bent Laue crystal monochromator, and Perkin-Elmer image plate detector mounted perpendicular to the primary beam. Finely pulverized sample packed in cylindrical polyimide capillary 1mm in diameter was placed 204 mm away from the detector. Multiple scans were performed to a total exposure time of 120 s. The 2D diffraction data were integrated and converted to intensity versus 2$\theta$ using the software FIT2D. The intensity data were corrected and normalized and converted to atomic pair distribution function (PDF), $G(r)$, using the program PDFgetX2. The average stoichiometry of SrFBiS$_2$ polycrystal was determined by examination of multiple points using an energy-dispersive x-ray spectroscopy (EDX) in a JEOL JSM-6500 scanning electron microscope.
C. Electrical and Thermal Transport Measurements.

The sample pellets were cut into rectangular bar and the surface is polished by sandpaper. Thin Pt wires were attached using silver epoxy for four probe resistivity measurements. Electrical and thermal transport measurements were carried out in Quantum Design Physical Property Measurement System (PPMS-9).

D. Band Structure Calculations.

First principle electronic structure calculation were performed using experimental crystallographic parameters within the full-potential linearized augmented plane wave (LAPW) method implemented in WIEN2k package. The general gradient approximation (GGA) of Perdew et al. was used for exchange-correlation potential. The LAPW sphere radius were set to 2.5 Bohr for all atoms, and the converged basis corresponding to $R_{\text{min}}k_{\text{max}} = 7$ with additional local orbital were used where $R_{\text{min}}$ is the minimum LAPW sphere radius and $k_{\text{max}}$ is the plane wave cutoff.

III. RESULTS AND DISCUSSION

A. Structure and Composition.

Fig. 1(a) shows the powder XRD pattern of SrFBiS$_2$ measured by Rigaku Miniflex. Almost all of reflections can be indexed using the P4/nmm space group. The unidentified peaks belong to the second phase of Bi$_2$S$_3$. Using two-phase Le Bail fitting, the refined lattice parameters of SrFBiS$_2$ are $a = 4.084(2)$ Å and $c = 13.798(2)$ Å. When compared to LaOBiS$_2$, the a-axial lattice parameter is larger and the c-axial one is slightly smaller. The PDF structural analysis was carried out using the program PDFgui. The SrFBiS$_2$ data are explained well within the model having P4/nmm symmetry with $a = 4.079(2)$ Å and $c = 13.814(5)$ Å ($R_{\text{wp}} = 0.138$, $\chi^2=0.024$). It is consistent with the fitting results obtained from Miniflex. The final fit is shown in Fig. 1(b), and the results are summarized in Table 1. In addition to the principal phase, the sample is found to have $\sim 16(1)$ wt% of Bi$_2$S$_3$ impurity with Pnma symmetry, which is also observed in Fig. 1(a). Structure of SrFBiS$_2$ is similar to LaOBiS$_2$, which is built up by stacking the rock-salt-type BiS$_2$ layer and fluorite-type SrF layer alternatively along the c axis as shown Fig. 1(c). The EDX spectrum of polycrystal confirms the presence of Sr, F, Bi, and S. The average atomic ratios determined from EDX are Sr : F : Bi : S = 1.00(4) : 1.00(9) : 1.03(5) : 1.88(4) when setting the content of Sr as 1. It confirms the formula of obtained compound is SrFBiS$_2$.

B. Electrical Properties.

As shown in Fig. 2, the resistivity $\rho(T)$ of SrFBiS$_2$ polycrystalline shows a semiconducting behavior in the measured temperature region (1.9-300 K). It should be noted that Bi$_2$S$_3$ polycrystal shows metallic behavior because of sulfur deficiency. The impurity may have some minor influence on the absolute value of resis-
TABLE I. Crystallographic Data for SrFBiS$_2$ obtained from synchrotron powder XRD.

| Chemical Formula | SrFBiS$_2$ |
|------------------|------------|
| Formula Mass (g/mol) | 379.73 |
| Crystal System | Tetragonal |
| Space Group | P4/nmm (No. 129) |
| \(a\) (Å) | 4.079(2) |
| \(c\) (Å) | 13.814(5) |
| \(V\) (Å$^3$) | 229.8(3) |
| \(Z\) | 2 |
| Density (g/cm$^3$) | 5.51 |

| Atom site | \(x\) | \(y\) | \(z\) | \(U_{eq}\) (Å$^2$)$^a$ |
|-----------|-------|-------|-------|-----------------|
| Sr 2c     | 1/4   | 1/4   | 0.1025(2) | 0.0069(4) |
| F 2a      | 3/4   | 1/4   | 0      | 0.033(2)   |
| Bi 2c     | 1/4   | 1/4   | 0.6286(5) | 0.0183(3) |
| S1 2c     | 1/4   | 1/4   | 0.379(3) | 0.060(2)   |
| S2 2c     | 1/4   | 1/4   | 0.811(2) | 0.019(1)   |

$^a$ \(U_{eq}\) is defined as one-third of the orthogonalized \(U_{ij}\) tensor.

FIG. 2. Temperature dependence of the resistivity \(\rho(T)\) of the SrFBiS$_2$ at \(H = 0\) (closed blue square) and 90 kOe (open red circle). Inset shows the fitted result using thermal activation model for \(\rho(T)\) at zero field where the red line is the fitting curve.

The temperature dependence of the resistivity, but the semiconducting behavior should be intrinsic. Neglecting the grain boundary contribution, the room-temperature resistivity \(\rho(300\,\text{K})\) is about 0.5 Ω·cm. Using the thermal activation model \(\rho_{ab}(T) = \rho_0 \exp(E_a/k_B T)\) (\(\rho_0\) is a prefactor, \(E_a\) thermal activated energy and \(k_B\) the Boltzmann’s constant) to fit the \(\rho(T)\) at high temperature (75 K - 300 K) (inset of Fig. 2), we obtain \(E_a = 31.8(3)\) meV. The semiconducting behavior is consistent with theoretical calculation result shown below. On the other hand, theoretical calculations have indicated that undoped LaOBiS$_2$ is also a semiconductor, which is partially consistent with the experimental result.\textsuperscript{13, 30} Transport measurement indicates that LaOBiS$_2$ shows semiconducting behavior at \(T < 200\) K, but exhibit an upturn of resistivity at higher temperature. The origin of the upturn is unclear. Therefore, the replacement of LaO by SrF should not change the band structure and thus physical properties too much, especially at low temperature, similar to the relation between SrFFeAs and LaOFeAs.\textsuperscript{18, 31} The slight differences between LaOBiS$_2$ and SrFBiS$_2$, such as larger \(a\)-axial and smaller \(c\)-axial lattice parameters, could result in changing of physical properties at higher temperature. Note that the semiconducting \(\rho(T)\) in LaOBiS$_2$ and SrFBiS$_2$ are different from those in parent compounds of iron pnictide superconductors. The latter show metallic behaviors at high temperature and semiconducting-like upturn in resistivity curve related to the spin density wave (SDW) transition. There is no significant magnetoresistance in SrFBiS$_2$ up to 90 kOe magnetic field.

C. Thermal Transport Properties.

The temperature dependences of the thermal conductivity \(\kappa(T)\) and thermolectric power (TEP) \(S(T)\) for SrFBiS$_2$ in zero field between 2 and 350 K are shown in Fig. 3. The electronic thermal conductivity \(\kappa_e(T)\) estimated from the Wiedemann-Franz law using a value for the Lorenz number of \(2.44 \times 10^{-8} \text{ W} / \text{K}^2\) was less than \(5 \times 10^{-6}\) of \(\kappa(T)\). Therefore, lattice thermal conductivity dominates \(\kappa_L(T)\) which exhibits a peak at around 60 K (Fig. 1(a)). The peak in \(\kappa(T)\) commonly arises since different phonon scattering processes usually dominate in different temperature ranges. Umklapp scattering dominates at high temperatures, while boundary and pointdefect scattering dominate at low and intermediate tem-
FIG. 3. Temperature dependence of (a) thermal conductivity and (b) thermoelectric power for SrFBiS$_2$ under zero magnetic field within a temperature range from 2 to 340 K.

**FIG. 4.** (a) Total and atom resolved density of states and (b) band structure of SrFBiS$_2$.

temperatures, respectively. On the other hand, the $\kappa(T)$ of SrFBiS$_2$ shows similar behavior to Bi$_4$O$_3$S$_3$ but with different peak position and absolute value. For TEP $S(T)$ of SrFBiS$_2$, there is a reversal in sign at about 11 K, i.e., hole-like carrier changes into electron-like carrier which is dominant at room temperature. According to two band model, $S = |S_h|\sigma_h - |S_e|\sigma_e/(\sigma_e + \sigma_h)$.

If we assume that $S_h$ and $S_e$ are temperature independent, it suggests that electron and hole conductivities change dramatically with temperature: at low temperature, $\sigma_h > \sigma_e$ whereas $\sigma_e > \sigma_h$ above 11 K. Hole-like carrier may originate from defect induced p-type doping. With increasing temperature, electron-like carrier due to intrinsic band excitation increase significantly, finally leading to $\sigma_e > \sigma_h$ and a sign change in $S(T)$. Similar behavior was observed in LaOZnP and p-type Si.

Even though the $S(T)$ in SrFBiS$_2$ is significant and not much smaller than in classics thermoelectric materials, its low electrical conductivity makes its figure of merit $ZT = \sigma S^2 T/\kappa$ extremely small.

**D. Electronic Structure.**

First principle calculations (Fig. 4) confirm that SrFBiS$_2$ is a semiconductor with a direct band gap of 0.8 eV located at X point. This is similar to LaOBI$_2$S$_2$ where the energy gap was found to be 0.82 eV. The calculation confirms the results of transport measurement. Similar to LaOBI$_2$S$_2$, both S 3p and Bi 6p states are located around the Fermi level (-2.0 to 2.0 eV) in SrFBiS$_2$. Thus there is a strong hybridization between S 3p and Bi 6p states. The absence of dispersion along $\Gamma-Z$ line suggests quasi two dimensional character of the band structure in SrFBiS$_2$ (Fig. 4(b)). In LaOBI$_2$S$_2$, F doping results in metallic states and superconductivity at low temperature. Main influence of F substitution is a carrier doping that shifts the Fermi level and has only minor effect on the lowest conduction band. Due to similarity between SrFBiS$_2$ and LaOBI$_2$S$_2$, new superconductors could be obtained by chemical substitution.

**IV. CONCLUSION**

In summary, we report a discovery of a new layered fluorosulfide SrFBiS$_2$. It contains NaCl-type BiS$_2$ layer similar to Bi$_4$O$_3$S$_3$ and Ln(O,F)BiS$_2$ superconductors. SrFBiS$_2$ polycrystals shows semiconducting behavior between 2 K and 300 K. We observe rather small thermal conductivity and large TEP with sign reversal at low temperature. Theoretical calculation confirms the semiconducting behavior and indicates similar DOS and band structure to undoped LaOBI$_2$S$_2$. Because of the similarity between SrFBiS$_2$ and the parent compound of BiS$_2$-based superconductors, it is of interest to investigate the doping effects on physical properties of SrFBiS$_2$. It could pave a way to new members in this emerging family of
BiS$_2$-based superconductors.

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