High-pressure studies of superconductivity in BiO$_{0.75}$F$_{0.25}$BiS$_2$

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MS received 15 September 2016; accepted 7 March 2017; published online 25 September 2017

Abstract. BiO$_{0.75}$F$_{0.25}$BiS$_2$ crystallizes in tetragonal CeOBiS$_2$ structure (S. G. P4/nmm). We have investigated the effect of pressure on magnetization measurements. Our studies suggest improved superconducting properties in polycrystalline samples of BiO$_{0.75}$F$_{0.25}$BiS$_2$. The $T_c$ in our sample is 5.3 K, at ambient pressure, which is marginal but definite enhancement over $T_c$ reported earlier (= 5.1 K). The upper critical field $H_{c2}(0)$ is greater than 3 T, which is higher than earlier report on this material. As determined from the $M$–$H$ curve, both $H_{c2}$ and $H_{c3}$ decrease under external pressure $P$ (0 ≤ $P$ ≤ 1 GPa). We observe a decrease in critical current density and transition temperature on applying pressure in BiO$_{0.75}$F$_{0.25}$BiS$_2$.

Keywords. Superconductivity; crystal structure; resistivity; high pressure magnetism.

1. Introduction

Crystal structure of the parent LnOBiS$_2$ (Ln = La, Ce, Pr, Nd and Yb) consists of double BiS$_2$ layers stacked alternately with an Ln$_2$O$_2$ blocking layer. These semiconducting materials were made superconducting by doping F at the O-site or by introducing M$^{4+}$ ions (M = Th, Hf, Zr and Ti) at the Ln$^{3+}$-site. This approach yielded materials with $T_c$ ~ 2.5–10 K [1–8].

Taking clue from the rare-earth-based oxypnictides superconductors, LnO-layer was replaced by SrF-layer, thereby generating a new material SrFBiS$_2$ [9]. Superconductivity was induced in SrFBiS$_2$, $T_c$ ~ 2.7–10 K, by doping it with Ln (Ln = La, Ce, Pr, Nd and Sm) at the Sr-site [9–12]. The parent phases, i.e., LnOBiS$_2$, SrFBiS$_2$ and BiOBiS$_2$, are known to be semiconducting [1,2,5,6,9,13]. EuFBiS$_2$, the Eu-analogue of SrFBiS$_2$, shows metallic conduction and becomes superconducting at 0.3 K without any doping. As a consequence of electron doping under ambient condition, Eu$_{1-x}$Ln$_x$FBI$_2$ shows increased $T_c$ ~ 2.2 K, and 10 K under pressure [14,15]. Ln$_{1-x}$F$_x$BiS$_2$ (Ln = La, Ce, Pr and Nd) [2,4,5,8] and Sr$_{1-x}$La$_x$FBI$_2$ [9] show abrupt increase in $T_c$ from ~2 to 10 K upon application of pressure [16–20].

The increase in $T_c$ of LaO$_{0.4}$F$_{0.6}$BiS$_2$ is accompanied by a structural phase transition from a tetragonal to a monoclinic (P2$_1$/m) structure observed from high-pressure X-ray diffraction (XRD) measurements [18]. This enhancement of $T_c$ could be related to the suppression of semiconducting behaviour in this material, which shows an increase in the density of charge carriers [16]. On the other hand Bi$_4$O$_4$S$_3$ exhibits $T_c$ = 4.5 K at ambient pressure, and it shows a decrease in $T_c$ down to 3 K upon applying pressure ~ 2 GPa [21]. Therefore, one can see the antagonistic pressure effects on the two classes of superconductors, i.e., on applying pressure the superconducting transition temperature $T_c$ decreases for the one with metallic normal state resistivity and increases for the systems possessing semiconducting-type normal state resistivity.

In the BiOBiS$_2$ phase, the two Bi atoms occupy two different crystallographic positions. One of them is present in the blocking layer and the other goes to the conduction layer. Shao et al [13] studied the effect of F doping at O-sites in BiOBiS$_2$. The optimum fluorine content of ~24% at O-sites resulted in the composition with maximum $T_c$ ~ 3.5 K. In another report [22], high-pressure annealing of the as-synthesized samples was carried out; $T_c$ of such materials is reported to be 5.1 K. We observe a significantly higher $T_c$ ~ 5.3 K in our sample of BiO$_{0.75}$F$_{0.25}$BiS$_2$. In view of such procedural change in the synthesis of the title material we have carried out detailed studies on this system, including the high-pressure magnetization studies.

2. Experimental

Polycrystalline sample of nominal composition BiO$_{0.75}$F$_{0.25}$BiS$_2$ was prepared by the solid-state sealed-tube method. The reactants BiF$_3$, Bi$_2$O$_3$, Bi$_2$S$_3$ and Bi metal were weighed and mixed in the stoichiometric ratio in an Ar-filled glove box with O$_2$ and H$_2$O content < 1 ppm. Bi$_2$S$_3$ was pre-synthesized.
by the reaction of the elements at 500°C for 15 h in vacuum. The mixture of reactants was pelletized and sealed in an evacuated quartz tube and heated at 430°C for 24 h followed by quenching in ice water. The product so obtained was sintered twice under the same heating condition to improve the phase purity. The product obtained was dark-black in colour and was stable in air. The phase purity of the sample was checked by powder XRD using Cu-Kα radiation and a Bruker D8 advance diffractometer. Rietveld refinement of the powder XRD data was carried out using the TOPAS software package [23]. Magnetization of the polycrystalline sample was studied at various applied pressures up to ∼1 GPa in the temperature range 2–300 K in an applied magnetic field of 10 Oe in ZFC mode using a vibrating sample magnetometer (VSM) option in the Physical Property Measurement System (PPMS, Quantum Design, USA). A mixture of Fluorinert FC 70 and FC 77 (1:1) was used as the pressure-transmitting medium. The ambient resistivity measurements in applied magnetic field were carried out in the temperature range 2–300 K using a conventional four-probe method in the PPMS-VSM.

3. Results and discussion

The powder XRD pattern of BiO$_{0.75}$F$_{0.25}$BiS$_2$ confirms the formation of a tetragonal CeOBiS$_2$-type phase [24] with space group $P4/nmm$ (#129) as shown in figure 1a. Minor impurity peaks corresponding to Bi$_2$S$_3$, Bi$_2$O$_3$ and Bi metal (total impurity content < 15%) were detected. The crystal structure of BiO$_{0.75}$F$_{0.25}$BiS$_2$, shown in figure 1b, comprises layers of edge-sharing tetrahedral Bi$_2$O$_2$ alternating with conducting square pyramidal Bi$_2$S$_2$-bilayers. Structural parameters were calculated by Rietveld fit to powder XRD data in the 2θ range 10–80°, results of which are shown in table 1. The determined lattice parameters $a = 3.9663(3)$ Å, $c = 13.730(2)$ Å and the cell volume $V = 215.99(4)$ Å$^3$ are quite close to those reported previously for BiO$_{0.75}$F$_{0.25}$BiS$_2$ [13]. They are smaller than those of the parent BiOBiS$_2$ ($a = 3.9744$ Å, $c = 13.7497$ Å and $V = 220.8$ Å$^3$) [13]. This decrease in the cell parameters indicates effective doping as the F$^{1—}$ ion is smaller than O$^{2—}$, showing clearly that F$^{1—}$ has replaced O$^{2—}$ ions. We carried out the compositional analysis of the sample using SEM–EDX. A typical SEM micrograph (figure 2) shows the presence of Bi- and S-element. The actual fractions of oxygen and fluorine could not be estimated by EDX measurements. The ratio of Bi and S elements was Bi$_{2.26}$F$_{0.26}$S$_{2.1}$, which is quite close to that of the nominal composition.

The zero-field temperature-dependent resistivity of BiO$_{0.75}$F$_{0.25}$BiS$_2$ in the temperature range 2–300 K is shown in figure 3. The room temperature resistivity is about 4 mΩ cm. The sample shows typical metallic conduction, and a sharp superconducting transition with $T_c$ at 5.3 K. The criterion of determining onset $T_c$ is shown in the lower left inset of figure 3. The lower right inset of figure 3 shows the field dependence of variable temperature resistivity. At zero magnetic fields the transition width is 1 K, which broadens considerably on applying field. The upper inset of figure 3 shows the $H-T$ phase diagram for BiO$_{0.75}$F$_{0.25}$BiS$_2$ corresponding to the temperature where the resistivity is 90 and 10% of the normal state resistivity. As the initial part of the plot does not follow the WHH curve, we do not apply the WHH formula in our case. However, we can infer from our plot that the eventual $H_c(0)$ would certainly be higher than (or equal to) 3 T. The previous report [13] shows that the value of the upper critical field
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Table 1. Refined lattice parameters for $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy (fixed)</th>
</tr>
</thead>
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<tr>
<td>Bi</td>
<td>2c</td>
<td>0.25</td>
<td>0.25</td>
<td>0.1087(7)</td>
<td>1</td>
</tr>
<tr>
<td>O/F</td>
<td>2a</td>
<td>0.75</td>
<td>0.25</td>
<td>0 0.75/0.25</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>2c</td>
<td>0.25</td>
<td>0.25</td>
<td>0.6301(1)</td>
<td>1</td>
</tr>
<tr>
<td>S1</td>
<td>2c</td>
<td>0.25</td>
<td>0.25</td>
<td>0.353(5)</td>
<td>1</td>
</tr>
<tr>
<td>S2</td>
<td>2c</td>
<td>0.25</td>
<td>0.25</td>
<td>0.827(4)</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 2. EDAX analysis for $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$ showing the presence of all elements. Inset shows the SEM micrograph of the same sample and the highlighted regions, at which the data were collected.

for $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$ is 1.95 T. We calculate the Ginzburg–Landau coherence length $\xi = \left(\frac{\Phi_0}{2\pi H_{c2}}\right)^{1/2}$, where $\Phi_0$ is the magnetic flux quantum and its value $\Phi_0 = 2.07 \times 10^{-7}$ G cm$^2$. The coherence length $\xi_{GL}(0)$ is estimated to be $\sim 85$ Å for $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$, which is lower than the values reported for $\text{BiS}_2$-based material [13,25].

In the $\rho(T, H)$ experiment, along with the lowering of $T_c$ we observe a broadening of the resistive transition on application of external magnetic field. This hints towards active role of thermal fluctuations of vortices in $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$. Thus, the movement of vortices is evident and it follows the same model of Arrhenius-type thermally activated behaviour described by the equation $\rho(T, H) = \rho_0 \exp(-U_0/k_BT)$ as discussed in literature [25]. The magnetic field dependence of the activation energy ($U_0$) is shown in figure 4. The inset of figure 4 shows the Arrhenius plot ($\ln(\rho)$ vs. $T^{-1}$). The inset shows that the electrical resistivity is thermally activated in the region of resistivity between 11 and 16 m$\Omega$ cm. The activation energy $U_0$ is calculated from the slope of the curve in this linear region using the afore-mentioned formula. The best fit to the experimental data yields the values of the activation energy $U_0/k_B \sim 89$ K (0 T) and is suppressed to $\sim 0.031$ K (3 T) for $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$. The value of activation energy in the absence of field is less than that reported for $\text{Bi}_4\text{O}_4\text{S}_4$ superconductor [25]. The gradual decrease in $U_0$ with increase in magnetic field (from $H = 0$ to 3 T) for $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$ superconductor suggests strong vortex pinning forces in the presence of an applied magnetic field.

The variation of DC magnetization as a function of temperature for $\text{BiO}_{0.75}\text{F}_{0.25}\text{BiS}_2$ is shown in figure 5. Magnetization measurements are carried out near the superconducting transition temperature, for both the field-cooled (FC) and zero-field-cooled (ZFC) modes in an applied field of 20 Oe.
A sharp diamagnetic signal at $T_c^{\text{onset}} \sim 5.3$ K is observed. This value matches well with the onset $T_c$ obtained in electrical resistivity measurement. On applying hydrostatic pressure ($0 < P < 1$ GPa), the diamagnetic signal shifts to lower temperature as shown in figure 6. We observe a similar effect of negative pressure dependence of $T_c$ by high-pressure magnetization measurements as seen in high-pressure resistivity studies [22]. In figure 7 we show how the superconducting hysteresis loop of the sample measured in an applied field $H$, where $-1500$ Oe $\leq H \leq +1500$ Oe, varies at various values of external pressure. The $M-H$ plot indicates type-II behaviour of the compound, with both $H_{c1}$ and $H_{c2}$ decreasing upon application of pressure. It is clear that the difference $M_+ - M_-$ at any given field decreases with the increase of pressure, implying that the critical current decreases as a function of applied pressure. We show in figure 8 the pressure effects on magnetic-field-dependent critical current density at 2.5 K. The critical current density $J_c$ at different pressures was calculated from the $M(H)$ plot as shown in figure 8. We used the Bean’s model [26], according to which $J_c = 20\Delta M/d$, where $\Delta M$ is the difference between the increasing and decreasing branch of magnetization at an applied field value and $d$ is the average grain size. Based on the afore-mentioned observation we tabulate our results showing decrease in $T_c$ and $J_c$ on applying pressure in BiO$_{0.75}$F$_{0.25}$BiS$_2$. 

Figure 4. The magnetic field ($H$) dependence of the activation energy ($U_0/k_B$). Inset shows Arrhenius plot of BiO$_{0.75}$F$_{0.25}$BiS$_2$ at low temperature.

Figure 5. Temperature-dependent DC magnetization at ambient pressure in the FC and ZFC modes for BiO$_{0.75}$F$_{0.25}$BiS$_2$ at 20 Oe.

Figure 6. Pressure dependence of DC magnetization as a function of varying temperature at 20 Oe. Inset shows the decrease in $T_c$ on applying external pressure.

Figure 7. Pressure dependence of isothermal magnetization as a function of applied magnetic field 1500 Oe at 2.5 K. $M_+$ and $M_-$ are respective values of magnetization at a given field $H$. $M_+ - M_-$ is a measure of critical current at a field $H$ and at pressure $P$. 

Figure 8. Pressure effects on magnetic-field-dependent critical current density at 2.5 K. The critical current density $J_c$ at different pressures was calculated from the $M(H)$ plot as shown in figure 8. We used the Bean’s model [26], according to which $J_c = 20\Delta M/d$, where $\Delta M$ is the difference between the increasing and decreasing branch of magnetization at an applied field value and $d$ is the average grain size. Based on the afore-mentioned observation we tabulate our results showing decrease in $T_c$ and $J_c$ on applying pressure in BiO$_{0.75}$F$_{0.25}$BiS$_2$. 
We obtained a superconducting transition temperature \( T_c \) = 5.3 K for BiO\(_{0.75}\)F\(_{0.25}\)BiS\(_2\) from resistivity measurements. The pressure-dependent magnetization measurements show a decrease in \( T_c \), which is consistent with earlier reports. We have measured the superconducting hysteresis loop as a function of magnetic field under various pressures and the upper critical field in BiO\(_{0.75}\)F\(_{0.25}\)BiS\(_2\) is found to be higher than the earlier report on this material. There is a gradual decrease in activation energy \( U_0/k_B \) with increase in magnetic field (from \( H = 0 \) to 3 T) for BiO\(_{0.75}\)F\(_{0.25}\)BiS\(_2\). We observe a decrease in \( J_c \) and \( T_c \) under applied external pressure.

### Acknowledgements

AKG thanks DST for providing financial support. ZH and GST thank UGC and CSIR, respectively, for a fellowship. GKS and SA acknowledge the DST, DRDO, BRNS and UGC (RFSMS-SRF-Meritorious fellowship) for their financial support.

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