FAST TRACK COMMUNICATION

Enhancement of superconductivity near the pressure-induced semiconductor–metal transition in the BiS$_2$-based superconductors LnO$_{0.5}$F$_{0.5}$BiS$_2$ (Ln = La, Ce, Pr, Nd)

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Received 27 August 2013
Published 25 September 2013
Online at stacks.iop.org/JPhysCM/25/422201

Abstract
Measurements of electrical resistivity were performed between 3 and 300 K at various pressures up to 2.8 GPa on the BiS$_2$-based superconductors LnO$_{0.5}$F$_{0.5}$BiS$_2$ (Ln = Pr, Nd). At lower pressures, PrO$_{0.5}$F$_{0.5}$BiS$_2$ and NdO$_{0.5}$F$_{0.5}$BiS$_2$ exhibit superconductivity with critical temperatures $T_c$ of 3.5 and 3.9 K, respectively. As pressure is increased, both compounds undergo a transition at a pressure $P_t$ from a low $T_c$ superconducting phase to a high $T_c$ superconducting phase in which $T_c$ reaches maximum values of 7.6 and 6.4 K for PrO$_{0.5}$F$_{0.5}$BiS$_2$ and NdO$_{0.5}$F$_{0.5}$BiS$_2$, respectively. The pressure-induced transition is characterized by a rapid increase in $T_c$ within a small range in pressure of ∼0.3 GPa for both compounds. In the normal state of PrO$_{0.5}$F$_{0.5}$BiS$_2$, the transition pressure $P_t$ correlates with the pressure where the suppression of semiconducting behaviour saturates. In the normal state of NdO$_{0.5}$F$_{0.5}$BiS$_2$, $P_t$ is coincident with a semiconductor–metal transition. This behaviour is similar to the results recently reported for the LnO$_{0.5}$F$_{0.5}$BiS$_2$ (Ln = La, Ce) compounds. We observe that $P_t$ and the size of the jump in $T_c$ between the two superconducting phases both scale with the lanthanide element in LnO$_{0.5}$F$_{0.5}$BiS$_2$ (Ln = La, Ce, Pr, Nd).

(Some figures may appear in colour only in the online journal)

1. Introduction

The recent discovery of the BiS$_2$-based superconductor Bi$_2$O$_2$S$_3$ by Mizuguchi et al [1, 2] with a superconducting critical temperature $T_c^{onset}$ of 8.6 K has generated much interest in a new family of BiS$_2$-based superconductors. The members of the class of novel BiS$_2$-based superconductors have layered crystal structures that consist of superconducting BiS$_2$ layers separated by blocking layers which act as charge reservoirs that dope the BiS$_2$ layers with charge carriers [1]. Experimental efforts on the BiS$_2$-based materials have focused on increasing the charge carrier concentration...
via chemical substitution within the blocking layer [3–12] as well as through a reduction of the unit cell volume via the application of an external pressure [13–16]. Recent studies of the Bi$_2$S$_3$-based compounds involving chemical substitution within the blocking layers have led to the discovery of the related superconductors LnO$_3$F$_{0.5}$BiS$_2$ (Ln = La, Ce, Pr, Nd, Yb) [4, 8–11, 15]. The compound LaO$_3$F$_{0.5}$BiS$_2$, synthesized under high pressure, has been reported by Mizuguchi et al. to have a $T_c$ of 10.6 K which exceeds that of Bi$_2$O$_2$S$_3$ [9]. In addition, the compounds with Ln = Ce, Pr, Nd, and Yb exhibit $T_c$ onset values of $\sim$3.0, 5.6, 4.3, and 5.3 K, respectively [4, 8, 10, 11]. More recent work demonstrates that chemical substitution of the tetravalent ions Th$^{4+}$, Hf$^{4+}$, Zr$^{4+}$ and Ti$^{4+}$ for trivalent La$^{3+}$ in LaOBiS$_2$ increases the charge carrier density and induces superconductivity [12].

Measurements of the pressure dependence of the electrical resistivity $\rho$ and the superconducting critical temperature $T_c$ have also recently been reported for several of these new compounds [13–16]. In this paper, we report the temperature dependence of the electrical resistivity $\rho$ from 3 to 300 K for the LnO$_3$F$_{0.5}$BiS$_2$ (Ln = Pr, Nd) compounds under applied quasi-hydrostatic pressure up to $\sim$2.8 GPa. Both compounds exhibit the same qualitative evolution of $T_c$ in which they undergo a pressure-induced transition at $P_1$ from a low $T_c$ superconducting phase to a high $T_c$ superconducting phase. This transition region is characterized by a rapid increase of $T_c$ in a narrow range of pressure $\sim$0.3 GPa. In the high $T_c$ phase at $\sim$2.5 GPa, we observed a maximum $T_c$ of 7.6 K for PrO$_3$F$_{0.5}$BiS$_2$ and 6.4 K for NdO$_3$F$_{0.5}$BiS$_2$. In the normal state of both materials, there is a significant suppression of semiconducting behaviour with pressure which is continuous up to the pressure $P_1$. A rapid increase of the charge carrier density is inferred from both the suppression of the semiconducting behaviour and the rapid increase of $T_c$ in this region [17].

The pressure dependence of $\rho$ and the evolution of $T_c$ reported in this paper for the LnO$_3$F$_{0.5}$BiS$_2$ (Ln = Pr, Nd) compounds are qualitatively similar to the behaviour recently reported for the LnO$_3$F$_{0.5}$BiS$_2$ (Ln = La, Ce) compounds [14]. For the four Bi$_2$S$_3$-based layered superconductors, LnO$_3$F$_{0.5}$BiS$_2$ (Ln = La, Ce, Pr, Nd), the transition pressure $P_1$ and the size of the ‘jump’ in $T_c$ between the two superconducting phases both scale with the lanthanide element Ln; specifically, as the atomic number of Ln increases, $P_1$ increases while the ‘jump’ in $T_c$ decreases.

2. Experimental section

Polycrystalline samples of LnO$_1$-$x$F$_x$BiS$_2$ (Ln = Pr, Nd) with $x = 0.5$ were prepared by solid-state reaction using powders of Pr$_2$O$_3$ (99.9%), PrF$_3$ (99.9%), Pr$_2$S$_3$ (99.9%), and Bi$_2$S$_3$ (99.9%) for PrO$_1$-$x$F$_x$BiS$_2$, and powders of Nd$_2$O$_3$ (99.9%), NdF$_3$ (99.9%), Nd$_2$S$_3$ (99.9%), and Bi$_2$S$_3$ (99.9%) for NdO$_1$-$x$F$_x$BiS$_2$. Bi$_2$S$_3$ precursor powder was prepared in an evacuated quartz tube by reacting Bi (99.99%) and S (99.9%) at 500°C for 10 h. The Ln$_2$S$_3$ (Ln = Pr, Nd) precursor powders were prepared in an evacuated quartz tube by reacting chunks of Pr and Nd with S grains at 800°C for 10 h. The starting materials with nominal composition LnO$_3$F$_{0.5}$BiS$_2$ (Ln = Pr, Nd) were weighed, thoroughly mixed, pressed into pellets, sealed in evacuated quartz tubes, and annealed at 800°C for 48 h. The products were ground, mixed for homogenization, pressed into pellets, and annealed again in evacuated quartz tubes at 800°C for 48 h. This last step was repeated again to promote phase homogeneity.

X-ray powder diffraction measurements (not shown) were made using an x-ray diffractometer with a Cu Kα source to assess phase purity and to determine the lattice parameters of the LnO$_3$F$_{0.5}$BiS$_2$ (Ln = Pr, Nd) compounds. The main diffraction peaks for the two samples can be well indexed to a tetragonal structure with space group $P4/nmm$ conforming to the CeOBiS$_2$ structure. The lattice parameters for PrO$_3$F$_{0.5}$BiS$_2$ were determined to be $a = b = 4.0192$ Å and $c = 13.4238$ Å, while for NdO$_3$F$_{0.5}$BiS$_2$ the lattice parameters are $a = b = 4.0102$ Å and $c = 13.4468$ Å [11].

Measurements of $\rho(T)$ under applied pressure were performed up to $\sim$2.8 GPa in a clamped piston cylinder pressure cell between ~3 and 300 K in a pumped He dewar. A 1:1 by volume mixture of n-pentane and isooamyl alcohol was used to provide a quasi-hydrostatic pressure transmitting medium. Annealed Pt leads were affixed to gold-sputtered contact surfaces on each sample with silver epoxy in a standard four-wire configuration. The pressure dependence of $T_c$ for high purity Sn (99.999%) was measured inductively and used as a manometer for the experiments. The pressure was determined by calibrating our $T_c$ data for Sn against data used in [18]. The width of the superconducting transition of the Sn manometer was used as a measure of the error in pressure, which was found to be on the order $\Delta P \sim \pm 0.05$ GPa.

3. Results

Plots of the temperature dependence of the electrical resistivity $\rho$ below 300 K for PrO$_3$F$_{0.5}$BiS$_2$ and NdO$_3$F$_{0.5}$BiS$_2$ at various pressures up to 2.8 GPa are shown in figures 1(a) and (b), respectively. Both compounds exhibit semiconducting behaviour at low pressure, indicated by a negative temperature coefficient of resistivity ($d\rho/dT < 0$). The semiconducting behaviour is strongly suppressed at lower pressures. As pressure is increased, the electrical resistivity $\rho$ of PrO$_3$F$_{0.5}$BiS$_2$ becomes weakly temperature dependent above $\sim$1.5 GPa, but remains semiconducting ($d\rho/dT < 0$). In contrast, the NdO$_3$F$_{0.5}$BiS$_2$ sample becomes metallic at $\sim$2 GPa, indicated by a positive temperature coefficient of resistivity ($d\rho/dT > 0$) in figure 1(b).

Superconducting transitions for PrO$_3$F$_{0.5}$BiS$_2$ and NdO$_3$F$_{0.5}$BiS$_2$ are displayed in figures 1(c) and (d), respectively. At lower pressures up to $\sim$1 GPa, the superconducting transitions in PrO$_3$F$_{0.5}$BiS$_2$ are grouped near 3.5 K. As pressure is increased, there is a slight broadening of the width of the superconducting transition $\Delta T_c$ at $\sim$1.5 GPa which is immediately followed by a dramatic increase in $T_c$ from ~3.9 to 7.4 K in the narrow range $\sim$1.5–1.8 GPa. Above 1.8 GPa, $T_c$ passes through a maximum of 7.6 K at $\sim$2.5 GPa and then gradually decreases.
with increasing pressure. We observed similar behaviour in the 
NdO$_{0.5}$F$_{0.5}$BiS$_2$ compound. Sharp superconducting
transitions near 4.0 K were observed at low pressures up to
$\sim$1.5 GPa. The width $\Delta T_c$ of the superconducting transition
then appears to broaden near 1.8 GPa. In the small range
$\sim$1.8–2.1 GPa, there is a sizeable increase in $T_c$ from 3.9
K to 6.4 K at 2.5 GPa and then decreases slowly with pressure.
In the NdO$_{0.5}$F$_{0.5}$BiS$_2$ compound, $T_c$ increases to a maximum
value of 7.6 K at 2.5 GPa and then steadily decreases with pressure,
while in the NdO$_{0.5}$F$_{0.5}$BiS$_2$ compound, $T_c$ increases
to a maximum value of 6.4 K at $\sim$2.5 GPa and then decreases
slowly with pressure.

In the normal state (above the $T_c(P)$ curves shown in
figure 2), the semiconducting behaviour in both compounds
is continuously suppressed with pressure as manifested by the
decrease of the energy gap $\Delta_1$ (defined below) with pressure,
the values of which are indicated in the false colour legend of
figures 2(a) and (b) for PrO$_{0.5}$F$_{0.5}$BiS$_2$ and
NdO$_{0.5}$F$_{0.5}$BiS$_2$ compounds. Sharp superconducting
phases for PrO$_{0.5}$F$_{0.5}$BiS$_2$, $T_c$ increases from 3.5 K to a maximum
of 7.6 K while in NdO$_{0.5}$F$_{0.5}$BiS$_2$, $T_c$ increases
from 3.9 K to a maximum of 6.4 K.

Figure 1. (a), (b) Temperature dependence of the electrical resistivity $\rho$ at various pressures for (a) PrO$_{0.5}$F$_{0.5}$BiS$_2$ and (b) NdO$_{0.5}$F$_{0.5}$BiS$_2$.
At lower pressures, both compounds exhibit semiconducting behaviour which is suppressed with increasing pressure. NdO$_{0.5}$F$_{0.5}$BiS$_2$ becomes completely metallic at $\sim$2 GPa ($\partial \rho / \partial T > 0$). (c), (d) Resistive superconducting transition curves for (c) PrO$_{0.5}$F$_{0.5}$BiS$_2$ and
(d) NdO$_{0.5}$F$_{0.5}$BiS$_2$ at various pressures. In PrO$_{0.5}$F$_{0.5}$BiS$_2$, $T_c$ increases from 3.5 K to a maximum of 6.4 K.

For the PrO$_{0.5}$F$_{0.5}$BiS$_2$ compound, $T_c$ increases dramatically
from 3.9 to 7.4 K as pressure is increased from $\sim$1.5 to
1.8 GPa ($dT_c/dP = 11.7$ K GPa$^{-1}$). In the NdO$_{0.5}$F$_{0.5}$BiS$_2$
compound, there is a significant jump in $T_c$ from 3.9 to 6.3 K
as pressure is increased from $\sim$1.8 to 2.1 GPa ($dT_c/dP = 8.0$ K GPa$^{-1}$). Following the rapid increase in $T_c$, $T_c$
gradually increases to its maximum value and then slowly
decreases with pressure. In the PrO$_{0.5}$F$_{0.5}$BiS$_2$ compound, $T_c$
increases to a maximum value of 7.6 K at 2.5 GPa and then
steadily decreases with pressure, while in the NdO$_{0.5}$F$_{0.5}$BiS$_2$
compound, $T_c$ increases to a maximum of 6.4 K at
$\sim$2.5 GPa and then decreases slowly with pressure.

In the normal state (above the $T_c(P)$ curves shown in
figure 2), the semiconducting behaviour in both compounds
is continuously suppressed with pressure as manifested by the
decrease of the energy gap $\Delta_1$ (defined below) with pressure,
the values of which are indicated in the false colour legend of
figures 2(a) and (b) for PrO$_{0.5}$F$_{0.5}$BiS$_2$ and NdO$_{0.5}$F$_{0.5}$BiS$_2$, respectively. The NdO$_{0.5}$F$_{0.5}$BiS$_2$ sample
exhibits a fully metallic state at $\sim$2 GPa (where $\Delta_1$ vanishes), represented by
the green region to the right of the crosshatching in figure 2(b).

From the plot of $\log(\rho)$ versus $P$ displayed in
figure 3(a), there is a noticeable change in the magni-
be described over two distinct temperature regions by the

\[ \rho(T) \text{ versus pressure in the normal state (plotted on a log scale). Values of } \rho \text{ for PrO}_{0.5}F_{0.5}BiS_2 \text{ and NdO}_{0.5}F_{0.5}BiS_2 \text{ were taken at } T = 8.5 \text{ and } 7.5 \text{ K, respectively. Dotted lines reflect the slopes (suppression rates), and arrows point to changing slopes at } \sim 2.1 \text{ GPa. The breaks in slope occur at the transition pressure } P_t. \text{ (b) Energy gap } \Delta_1 \text{ (} \sim 100-200 \text{ K) versus pressure for both compounds. The rate of decrease in } \Delta_1 \text{ with pressure flattens at } \sim 2 \text{ GPa in both compounds. Above } \sim 1.9 \text{ GPa, } \Delta_1/k_B = 0 \text{ K in NdO}_{0.5}F_{0.5}BiS_2. \]

relation \( \rho(T) = \rho_0 e^{\Delta/k_B T} \) where \( \rho_0 \) is a constant and \( \Delta \) is an energy gap. In a recent paper, we applied this analysis to extract the high and low temperature energy gaps \( \Delta_1 \) and \( \Delta_2 \) for the LnO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) (Ln = La, Ce) compounds [14]. We used the same analysis in the current study to determine the value of the high temperature energy gap \( \Delta_1 \) for both compounds LnO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) (Ln = Pr, Nd). The energy gap \( \Delta_1 \) in NdO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) was determined using the \( \rho(T) \) data from the region 100–200 K for lower pressures 0.37–0.69 GPa and \( \rho(T) \) data from the region 20–100 K for higher pressures 1.47–2.80 GPa. For PrO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\), the energy gap \( \Delta_1 \) was extracted using \( \rho(T) \) data in the region 200–280 K for all pressures up to 2.80 GPa.

The pressure dependence of the energy gap \( \Delta_1 \) for both compounds is shown in figure 3(b). The energy gap \( \Delta_1 \) decreases rapidly with pressure up to \( \sim 2 \) GPa. Above \( \sim 2 \) GPa, \( \Delta_1 \) exhibits relatively little pressure dependence. This is consistent with the transition to a weaker suppression rate shown in figure 3(a) which also sets in at \( \sim 2 \) GPa. In NdO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\), the energy gap \( \Delta_1/k_B = 0 \) K above 1.8 GPa.
This is consistent with the semiconductor–metal transition near 2 GPa indicated by a positive temperature coefficient of electrical resistivity (d\(\rho\)/dT > 0) seen in the \(\rho(T)\) data shown in figure 1(b). The rapid decrease in the energy gap \(\Delta_1\) for \(P < P_t\) in both the \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) (\(\text{Ln} = \text{Pr, Nd}\)) compounds is similar to behaviour observed previously in the \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) (\(\text{Ln} = \text{La, Ce}\)) compounds [13, 14].

4. Discussion

Both the temperature dependence of the electrical resistivity \(\rho\) and the evolution of \(T_c\) under applied pressure for the \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) (\(\text{Ln} = \text{Pr, Nd}\)) samples reported in section 3 of this paper are markedly similar to the results we recently reported for the \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) (\(\text{Ln} = \text{La, Ce}\)) compounds [14]. As shown in the phase diagrams displayed in figure 4(a), each of the four compounds \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) (\(\text{Ln} = \text{La, Ce, Pr, Nd}\)) exhibits an abrupt pressure-induced transition from a low \(T_c\) superconducting phase at lower pressure to a high \(T_c\) superconducting phase at higher pressure.

In the four compounds, the pressure-induced transition observed in the superconducting state is coincident with changes in the suppression of the electrical resistivity \(\rho\) in the normal state. The rate of suppression of semiconducting behaviour (figure 3(a)) and the rate of decrease in the energy gap \(\Delta_1\) (figure 3(b)) both saturate at pressures that correlate with the transition pressure \(P_t\) into the high \(T_c\) superconducting phase. In the specific case of the \(\text{NdO}_{0.5}\text{F}_0.5\text{BiS}_2\) compound, a semiconductor–metal transition occurs at \(P_t\). These changes in the normal state electrical resistivity indicate there may be significant increases in the charge carrier density during the rapid increase in \(T_c\) that occurs between the two superconducting phases [17].

The transition pressures \(P_t\), indicated by the black arrows in the temperature–pressure phase diagrams of figure 4(a), were defined as the pressure corresponding to the value of \(T_c\) at the midpoint between the values of \(T_c\) in the low and high \(T_c\) phases immediately preceding and following the transition. \(P_t\) is plotted as a function of lanthanide element (\(\text{Ln} = \text{La, Ce, Pr, Nd}\)) in \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) in figure 4(b). There is a clear linear relationship between the increasing atomic number of \(\text{Ln}\) and an increase in \(P_t\). The magnitude of the ‘jump’ in \(T_c\) also scales with the atomic number of the \(\text{Ln}\) element in \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) as clearly shown in the inset of figure 4(b). The pressure-induced increase in \(T_c\) decreases in magnitude as the atomic number of the lanthanide element increases. The lengths of the vertical bars in figure 4(b) represent the respective pressure windows over which the transitions from the low \(T_c\) phase to the high \(T_c\) phase occurred in each of the four compounds. The pressure range over which the transition occurs also decreases with increasing atomic number of \(\text{Ln}\) in \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\). Table 1 contains values of low \(T_c\), maximum \(T_c\), overall increase in \(T_c\) (max. \(T_c\)—low \(T_c\)), and transition pressure \(P_t\), for each compound.

The evolution of \(T_c\) with pressure in the low \(T_c\) phase has recently been reported for the \(\text{LnO}_{0.5}\text{F}_0.5\text{BiS}_2\) (\(\text{Ln} = \text{Pr, Nd}\)) compounds in two studies by Selvan et al [15, 16].

For \(\text{PrO}_{0.5}\text{F}_0.5\text{BiS}_2\), they observed a gradual increase of \(T_c\) from 3.7 to 4.7 K with pressure up to \(\sim 2.2\) GPa [16]. For \(\text{NdO}_{0.5}\text{F}_0.5\text{BiS}_2\), they found a gradual evolution of \(T_c\) with pressure from 4.6 to 5.0 K up to a pressure of \(\sim 1.3\) GPa and then down from 5.0 to 4.8 K upon further application of pressure up to \(\sim 1.8\) GPa [15]. In both reports, however, there was no evidence of a transition characterized by a rapid increase in \(T_c\). It is possible that slight variations in the chemical composition of the samples in their studies compared to those studied by us may be responsible for
differences in the material’s response to applied pressure. Furthermore, the pressure transmitting media used in this study (see section 2) and the transmitting fluid used in their studies [15, 16] may have different properties with regard to pressure gradients that can affect the measured pressure at which a transition occurs [19]. It is also possible that the pressures reached in their studies were lower than the pressure required to induce the transitions that we observed in this report.

5. Concluding remarks

We have observed markedly similar behaviour in both the temperature dependence of the normal state electrical resistivity and also the evolution of the superconducting critical temperature \( T_c \) under applied pressure for the two BiS\(_2\)-based superconductors LnO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) (Ln = Pr, Nd). The qualitative behaviour observed for the two compounds in this study is strikingly similar to the results we recently reported for the two BiS\(_2\)-based superconductors LnO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) (Ln = La, Ce) [14]. In each of the four compounds LnO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) (Ln = La, Ce, Pr, Nd), there is a sizeable enhancement of \( T_c \) in the superconducting state accompanying the suppression of semiconducting behaviour with pressure in the normal state. The suppression of the semiconducting behaviour in the normal state saturates at a critical pressure \( P_1 \) which corresponds to the pressure where there is a transition between a low \( T_c \) superconducting phase and a high \( T_c \) superconducting phase. The semiconducting behaviour of the electrical resistivity in the normal state is consistent with an energy gap that is suppressed with pressure in a similar way. In the particular case of the NdO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) compound, there is a pressure-induced semiconductor–metal transition at \( P_1 \approx 2 \) GPa.

The coincidence of the saturation of the suppression of semiconducting behaviour in the normal state electrical resistivity with the rapid increase in \( T_c \) indicates there may be significant increases in the charge carrier density in the vicinity of the pressure-induced transition. We found that the transition pressure \( P_1 \) (see section 4) increases with increasing atomic number of the lanthanide element (Ln = La, Ce, Pr, Nd) in LnO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\). However, the size of the increase in \( T_c \) between the two superconducting phases decreases as lanthanide atomic number increases. The scaling of both the transition pressure \( P_1 \) and the size of the ‘jump’ in \( T_c \) with the atomic number of the lanthanide element suggests that the pressure-induced transition between the two superconducting phases may be a structural transition; however, at present, the precise mechanism driving the enhancement of \( T_c \) with pressure is unknown. X-ray diffraction experiments under pressure on the LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) compound are currently underway to help determine whether the pressure-induced enhancement of \( T_c \) and the suppression of semiconducting behaviour are related to a structural transition.

Acknowledgments

The authors thank A J Friedman for his helpful work in the synthesis of the LnO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) (Ln = La, Ce, Pr, Nd) compounds. High pressure research at the University of California, San Diego (UCSD) was supported by the National Nuclear Security Administration under the Stewardship Science Academic Alliance Program through the US Department of Energy (DOE) under Grant No. DE-NA0001841. Sample synthesis at UCSD was sponsored by the US Air Force Office of Scientific Research under MURI Grant No. FA9550-09-1-0603. Characterization of samples at ambient pressure was supported by the US DOE Grant No. DE-FG02-04-ER46105.

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