Mn-doping induced ferromagnetism and enhanced superconductivity in Bi$_{4-x}$Mn$_x$O$_4$S$_3$ (0.075 $\leq x \leq 0.15$)

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We demonstrate that Mn-doping in the layered sulfides Bi$_4$O$_4$S$_3$ leads to stable Bi$_{4-x}$Mn$_x$O$_4$S$_3$ compounds that exhibit both long-range ferromagnetism and enhanced superconductivity for 0.075 $\leq x \leq 0.15$, with a possible record superconducting transition temperature ($T_c$) $\sim$ 15 K amongst all BiS$_2$-based superconductors. We conjecture that the coexistence of superconductivity and ferromagnetism may be attributed to Mn-doping in the spacer Bi$_2$O$_2$ layers away from the superconducting BiS$_2$ layers, whereas the enhancement of $T_c$ may be due to excess electron transfer to BiS$_2$ from the Mn$^{4+}$/Mn$^{3+}$-substitutions in Bi$_2$O$_2$. This notion is empirically corroborated by the increased electron-carrier densities upon Mn doping, and by further studies of the Bi$_{4-x}$A$_x$O$_4$S$_3$ compounds ($A$ = Co, Ni; $x$ = 0.1, 0.125), where the $T_c$ values remain comparable to that of the undoped Bi$_2$O$_2$S$_3$ system ($\sim$ 4.5 K) due to lack of 4+ valences in either Co or Ni ions for excess electron transfer to the BiS$_2$ layers. These findings therefore shed new light on feasible pathways to enhance the $T_c$ values of BiS$_2$-based superconductors, although complete elucidation of the interplay between superconductivity and ferromagnetism in these anisotropic layered compounds awaits the development of single crystalline materials for further investigation.

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I. INTRODUCTION

One of the commonalities among the cuprate and iron-based high-temperature superconductors is their layered structures. Interestingly, even for conventional superconductors, the highest superconducting transition temperature ($T_c$) has been found in layered magnesium diboride MgB$_2$. Recently, superconductivity with $T_c = 4.5$ K was discovered in a new superconductor Bi$_4$O$_4$S$_3$. This compound has a layered structure composed of two superconducting BiS$_2$ layers and spacer layers of Bi$_4$O$_4$(SO$_4$)$_{1-x}$, where $x$ indicates the deficiency of (SO$_4$)$^{2-}$ ions at the interlayer sites. Since the discovery of Bi$_4$O$_4$S$_3$, several other Bi$_2$S$_2$-based superconductors LnO$_{1-x}$F$_x$BiS$_2$ (Ln = La, Ce, Pr, Nd) with the highest $T_c \sim 10.6$ K have been reported. Both experimental and theoretical studies to date have indicated that the BiS$_2$ layers play the role of the superconducting planes in these sulfide superconductors, similar to the CuO$_2$ planes in the cuprate superconductors and the Fe$_2$O$_2$ layers (A$^+$ = P, As, Se, Te) in the iron-based superconductors.

A major challenge facing this new class of layered superconductors is to optimize $T_c$ by exploring different spacer layers. Additionally, the effects of doping by either non-magnetic or magnetic elements are important issues for investigation. To date, suppression of superconductivity has been observed in the case of Cu and Ag substitutions for Bi in the Bi$_4$O$_4$S$_3$ superconductor, whereas coexistence of superconductivity and ferromagnetism has been reported in the CeO$_{1-x}$F$_x$BiS$_2$ and Sr$_{0.5}$Ce$_{0.5}$FBiS$_2$ systems at low temperatures. However, none of these doping effects are fully understood.

Aiming at addressing the aforementioned issues, we report in this work our studies of 3d transition-metal substitutions for Bi in Bi$_4$O$_4$S$_3$ by synthesizing Bi$_{4-x}$A$_x$O$_4$S$_3$ ($A$ = Mn, Co, Ni; 0.075 $\leq x \leq 0.15$) compounds with conventional solid state reaction. We first focus on the investigation of Bi$_{4-x}$Mn$_x$O$_4$S$_3$ because these results are most interesting and reveal a possible record $T_c \sim 15$ K, and then perform comparative studies on Bi$_{4-x}$A$_x$O$_4$S$_3$ ($A$ = Co, Ni) in the Discussion section to elucidate the underlying physics. Based on our empirical findings, we suggest that the coexistence of superconductivity and long-range ferromagnetism in all Bi$_{4-x}$A$_x$O$_4$S$_3$ ($A$ = Mn, Co, Ni) compounds may be attributed to the selective doping of 3d transition-metal elements in the spacer Bi$_2$O$_2$ layers, whereas the enhancement of $T_c$ found only in Mn-doped samples may be due to substan-

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tial electron transfer from Mn$^{4+}$/Mn$^{3+}$-substitutions in Bi$_2$O$_2$ to the superconducting BiS$_2$ layers.

II. EXPERIMENTAL

Bulk polycrystalline Bi$_{4-x}$Mn$_x$O$_4$S$_3$ (x = 0.075, 0.1, 0.125, 0.15) and Bi$_{1-x}$A$_x$O$_4$S$_3$ (A = Co, Ni; x = 0.1, 0.125) samples were synthesized by conventional solid state reaction method. For the Bi$_{4-x}$Mn$_x$O$_4$S$_3$ samples, high purity Bi (99.99%), Bi$_2$O$_3$ (99.99%), S (99.999%), MnO$_2$ (99.99%) were first weighed in stoichiometric ratio and then grounded thoroughly in a glove box under high purity argon atmosphere. Next, the mixture was pressed into a pellet shape and sealed in an evacuated quartz tube ($10^{-4}$ Torr). The pellet was then heated up to 510 °C and kept for 10 hours. After cooling the pellet to room temperature, the product was well mixed again by regrinding, pressed into a pellet shape, and then annealed at 510 °C for another 10 hours. The samples thus obtained looked black and were hard. It is important to note that the sample may not be heated above 550 °C. Otherwise S-O gas would be produced and could result in explosion of the quartz tube. Similar procedures were applied to the synthesis of the Bi$_{4-x}$A$_x$O$_4$S$_3$ (A = Co, Ni; x = 0.1, 0.125) samples.

The crystal structures of all samples were characterized by X-ray powder diffraction (XRD, 18 kW D/Max 2550) using the Cu-K$_\alpha$ radiation. The lattice constants were calculated from the 2θ values and the Miller indices by using the Jade 6.5 software. After XRD studies, these polycrystalline samples were cut into rectangular shape and polished for electrical resistivity measurements. The electrical resistivity was measured with a standard four-terminal method covering temperature range from 3 to 300 K in a Physical Property Measurement System (PPMS-9, Quantum Design, Inc.). Typical current densities used for the resistive measurements were ~ 100 A/m$^2$. No apparent dependence on the current density was found up to ~ 2000 A/m$^2$, whereas resistive signals became difficult to resolve for current densities significantly smaller than 100 A/m$^2$. The magnetization and specific heat measurements were conducted using the same PPMS with Vibrating Sample Magnetometer (VSM) and specific heat options. The zero-field-cooling (ZFC) and field-cooling (FC) of the magnetic susceptibility measurements of the samples were performed in the warming process. Additionally, the carrier densities of bulk polycrystalline samples were determined from their normal-state Hall coefficients at 300 K by means of the van der Pauw method and with the use of the Hall Effect Measurement System CVM200 made by the East Changing Company.

III. RESULTS AND ANALYSIS

A. Structural characterization

The XRD patterns of different Mn-doped samples and the corresponding crystalline structure are shown in Fig. 1(a)-(b). These data suggest that all samples acquired the expected tetragonal phase (space group I4/mmm) with minor rhombohedra Bi$_2$S$_3$ and Bi impurities, the latter being common occurrences in the Bi$_2$O$_3$ system and exhibiting no superconductivity above 3 K. The nominal Mn-doping (x) dependence of the lattice constants a and c are illustrated in the inset of Fig. 1(a). The general trend of decreasing lattice parameters with increasing Mn-doping is reasonable because the ionic radii of Mn are much smaller than that of Bi$^{3+}$. This trend is also indicative of successful incorporation of Mn-ions into the Bi$_2$O$_3$S$_3$ unit cells. Similarly, the lattice constants of Bi$_{1-x}$A$_x$O$_4$S$_3$ (A = Co, Ni) also indicate that the lattice constants of Bi$_{1-x}$A$_x$O$_4$S$_3$ were all reduced relative to those of Bi$_2$O$_3$S$_3$, as shown in Fig. 1(c). Moreover, the lattice constants for different dopants followed the descending order of Co, Ni and Mn, as explicitly shown in the inset of Fig. 1(c).

B. M-vs.-T and ρ-vs.-T studies of Bi$_{4-x}$Mn$_x$O$_4$S$_3$

Temperature (T) dependent magnetization (M) of Bi$_{4-x}$Mn$_x$O$_4$S$_3$ with x = 0.075, 0.10, 0.125 and 0.15 was studied under both zero-field-cool (ZFC) and field-cool (FC) conditions from 3 to 300 K and with an external field H = 100 Oe, as illustrated in Fig. 2. For each magnetization curve, three characteristic temperatures are noteworthy: The Neél temperature (T$_N$) near ~ 125 K for x = 0.125 and 0.15, below which M decreased due to the onset of antiferromagnetism; the Curie temperature (T$_{Curie}$) near ~ 50 K for all samples, below which a rapid upturn followed by saturation in the FC magnetization curves appeared, suggesting the formation of long range ferromagnetism; and the temperature T$_{c,M}$ ~ 4.5 K below which rapid decrease in magnetization occurred as the result of supercurrent-induced diamagnetism. Additionally, we note the dramatic contrasts between the ZFC and FC magnetization curves for T$_{c,M}$ < T < T$_{Curie}$ in all samples: The ZFC curves all exhibited an initial upturn of magnetization, signaling the onset of ferromagnetism, which was followed by gradual decrease and then a sharp downturn in magnetization. Interestingly, both the diamagnetic contribution in the ZFC curve and the magnitude of ferromagnetism in the FC curve increased with increasing x.

To better understand the interplay of magnetism and superconductivity, we conducted measurements of resistivity (ρ) vs. T on Bi$_{4-x}$Mn$_x$O$_4$S$_3$. As shown in Fig. 3(a), all samples reached zero resistance at low temperatures. On the other hand, the resistivity of samples with lower Mn-doping levels (x = 0.075, 0.10) exhibited monotonic
The highly anisotropic, layered nature of these BiS$_2$-based compounds, the physical origin for this doping dependent resistive upturn cannot be fully uncovered without the availability of single crystalline materials. Nonetheless, a feasible mechanism that contributes to the resistive upturn is the occurrence of Kondo resonance at $T < T_K$, where $T_K$ denotes the Kondo temperature. In this scenario, a lower $T_K$ for a sample with a higher Mn-doping level would be consistent with stronger ferromagnetism and a sharper Kondo resonance of a linewidth $\sim T_K/2$. Moreover, the formation of Kondo clouds below $T_K$ could help screen localized magnetic moments and so would be important to the appearance of singlet superconductivity, because the coexistence of ferromagnetism and superconductivity would obscure the onset of the Meissner effect. Similarly, the polycrystalline nature of our Bi$_{1-x}$Mn$_x$O$_4$S$_3$ samples could significantly reduce the $T_{c,\rho}$ values below the intrinsic superconducting transition temperature $T_c$ because of the inter-granular weak-link effects. Hence, additional thermodynamic measurements of $M$-vs.-$H$ at $T < T_{Curie}$ and specific heat ($C$)-

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**FIG. 1.** (Color online) Structural properties of Bi$_{4-x}$A$_x$O$_4$S$_3$ (A = Mn, Co, Ni): (a) X-ray diffraction (XRD) patterns of Bi$_{4-x}$Mn$_x$O$_4$S$_3$ (0.075 $\leq x \leq 0.15$). The inset shows the doping dependent variations of the in-plane and c-axis lattice parameters $a$ and $c$. (b) Schematics of the layered structure of Bi$_{4-x}$Mn$_x$O$_4$S$_3$. (c) X-ray diffraction (XRD) spectral studies of Bi$_{4-x}$Co$_x$O$_4$S$_3$ and Bi$_{4-x}$Ni$_x$O$_4$S$_3$ for $x = 0.125$. The XRD spectra indicated that the lattice constants after 3d transition-metal doping were all reduced relative to those of Bi$_4$O$_4$S$_3$, and the values for different dopants followed the descending order of Co, Ni and Mn, as shown in the inset of (c).

**FIG. 2.** (Color online) Temperature dependent magnetization of Bi$_{1-x}$Mn$_x$O$_4$S$_3$ ($x = 0.075$, 0.10, 0.125, 0.15): Zero-field-cool (ZFC) and field-cool (FC) magnetization as a function of $T$ is shown in the main panel from 3 to 300 K with an external field $H = 100$ Oe. For each magnetization curve, three characteristic temperatures are noteworthy: The Néel temperature ($T_N$) near $\sim 125$ K for $x = 0.075$, 0.10 and 0.125; the Curie temperature ($T_{Curie}$) near $\sim 50$ K; and the magnetization-determined superconducting transition temperature ($T_{c,M}$). The inset shows an expansion of the main panel over the temperature range where strong contrasts appear between the ZFC and FC curves.

Temperature dependence up to 150 K, whereas a resistive upturn appeared at $\sim 55$ K and $\sim 23$ K for higher Mn-doping levels $x = 0.125$ and 0.15, respectively. Given the highly anisotropic, layered nature of these BiS$_2$-based
FIG. 3. (Color online) Characterization of the superconducting transition temperatures of Bi$_{4-x}$Mn$_x$O$_4$S$_3$: (a) Resistivity ($\rho$) vs. temperature ($T$) behavior of Bi$_{4-x}$Mn$_x$O$_4$S$_3$. The inset is the enlargement of the lower temperature regime for $x = 0.125$ and 0.15, showing Kondo-like resistive upturn at $T \sim 55$ K for $x = 0.125$ and at $T \sim 23$ K for $x = 0.15$. (b) Detailed $\rho$-vs.-$T$ curves of all samples near the onset of resistive superconducting transition ($T_{c,\rho}$), where $T_{c,\rho}$ (in units of K) exhibits slight decrease with increasing $x$. (c) ZFC-magnetization vs. $T$ behavior under $H = 100$ Oe and near $T_{c,\rho}$ (in units of K). (d) Comparison of the Mn-doping level dependence of $T_{c,\rho}$ from resistive data and $T_{c,M}$ from magnetization measurements.

vs.-$T$ studies in both zero and finite magnetic fields were necessary to unravel the true $T_c$ values of Bi$_{4-x}$Mn$_x$O$_4$S$_3$.

C. $M$-vs.-$H$ studies of Bi$_{4-x}$Mn$_x$O$_4$S$_3$

In Fig. 4(a) and (b) we show the hysteretic $M$-vs.-$H$ loops for $x = 0.125$ at low and high temperatures, respectively. Specifically, the low-temperature behavior in Fig. 4(a) with $T = 3, 7, 12$ and 14 K refers to the appearance of anomalous features associated with each magnetic hysteresis loop. These features diminished with increasing $T$. In contrast, the high-temperature behavior as manifested in Fig. 4(b) for the $M$-vs.-$H$ loop at $T = 20$ K reveals a standard magnetic hysteresis loop for a ferromagnetic material. We attribute the difference between the low- and high-temperature behaviors to the onset of superconductivity in the former. Specifically, we consider a standard although much smaller superconducting magnetization loop superposed on top of the ferromagnetic hysteretic loop. Both the isothermal ascending and descending branches of the $M$-vs.-$H$ loop at $T < T_c$ would deviate from the typical ferromagnetic hysteresis loop due to the presence of supercurrents. Hence, by considering the derivative $dM/dH$ of either the ascending or descending branch of the $M$-vs.-$H$ curve at a constant $T$, we expect one peak associated with the inflection point of a standard ferromagnetic $M$-vs.-$H$ curve at $T < T_c < T_{Curie}$. In contrast, an additional peak in the $dM/dH$ vs. $H$ curve is expected near $H = 0$ for $T < T_c$ because of the appearance of supercurrents, which is indeed confirmed by the data shown in Fig. 4(c).

We may define the magnetic field difference between the two peaks in $dM/dH$ as $\Delta H^* (T)$, which is a measure of the supercurrent. Therefore, we expect $\Delta H^* (T)$ to decrease with increasing $T$ and vanish at $T \sim T_c$, which is consistent with the empirical finding shown in Fig. 4(d), where $\Delta H^* (T)$ approaches 0 at $T = (16 \pm 2)$ K for $x = 0.125$. Similar behavior has also been confirmed for $x = 0.10$ and 0.15, as shown in Fig. 5(a)-(d).
These results suggest that \( T_c \sim (16 \pm 2) \) K for x = 0.10, 0.125 and 0.15, whereas the \( \Delta H^* \) values from the \( dM/dH \) curves for x = 0.075 have been difficult to determine due to significantly smaller M-vs.-H loops.

Our attribution of the anomalies in M-vs.-H loops of Bi\(_{4-x}\)Mn\(_x\)O\(_4\)S\(_3\) to superconductivity can be further corroborated by studies of the M-vs.-H loops of a related system Bi\(_{4-x}\)Co\(_x\)O\(_4\)S\(_3\) with x = 0.125. As we shall elaborate further in the Discussion section, the Bi\(_{3.875}\)Co\(_{0.125}\)O\(_4\)S\(_3\) compound is also a superconductor with \( T_c \sim 4.8 \) K and long-range ferromagnetism at low temperatures. Therefore, the M-vs.-H loops of Bi\(_{3.875}\)Co\(_{0.125}\)O\(_4\)S\(_3\) also revealed anomalies induced by superconducting persistent currents at \( T < T_c \), as shown in Fig. 3(b). On the other hand, the ferromagnetism in Bi\(_{3.875}\)Co\(_{0.125}\)O\(_4\)S\(_3\) was much weaker than that of Bi\(_{4-x}\)Mn\(_x\)O\(_4\)S\(_3\) (to be detailed in the Discussion section) so that the superconducting contributions in the M-vs.-H loops could be much better revealed. As exemplified in Fig. 3(b), the M-vs.-H loop of Bi\(_{3.875}\)Co\(_{0.125}\)O\(_4\)S\(_3\) taken at \( T = 3 \) K < \( T_c \) ~ 4.8 K could be decomposed into the superposition of a ferromagnetic loop and a superconducting loop. Moreover, we note that the superconducting contribution thus derived from the M-vs.-H data of Bi\(_{4-x}\)Co\(_x\)O\(_4\)S\(_3\) was in good agreement with the total M-vs.-H loop found in the non-magnetic, superconducting parent compound Bi\(_4\)O\(_4\)S\(_3\). These results therefore reaffirmed our notion that the hysteretic M-vs.-H loops of Bi\(_{4-x}\)A\(_x\)O\(_4\)S\(_3\) (A = Mn, Co, Ni) consisted of contributions from both superconductivity and ferromagnetism.
obtained from the $dM/dH$ curve taken at $T = 0.075, 0.10, 0.125$ and $0.15$ are respectively illustrated in Fig. 5 (a)-(d) and further detailed in Fig. 5 (e)-(h). We find that a sharp and asymmetric feature appeared near $T \sim 15$ K for all curves taken at $H = 0$. If we attribute the temperature where maximum $dC/dT$ appeared to $T_c$, the $T_c$ values were found to be nearly doping independent ($T_c \sim 15$ K), consistent with the results obtained from the $dM/dH$ studies in Figs. 4 and 5. This finding of $T_c \sim 15$ K is the highest superconducting transition temperature reported to date among the BiS$_2$-based superconductors.

We further note that the peak position of each $(dC/dT)$ curve taken at $H = 7$ T exhibited a small (0.3 $\sim$ 0.5 K) downshift relative to that taken at $H = 0$ (Fig. 7 (e)-(h)), and the peak height also diminished with magnetic field. The small downshift of the peak position at $H = 7$ T is suggestive of a relatively strong upper critical field $H_{c2}(0)$. Using the Werthamer-Helfand-Hohenberg (WHH) theory for the upper critical field, we find that the formula $H_{c2}(0) = -0.69T_c(dH_{c2}(T)/dT)|_{T_c}$ for $T \rightarrow T_c$ yields $H_{c2}(0)$ values in the range of $145 \sim 240$ T if we take $T_c = 15$ K.

Although the errors for these $H_{c2}(0)$ estimates are likely significant because of our limited specific heat data, we note that the $H_{c2}(0)$ value of the parent compound BiO$_3$S$_3$ with $T_c = 4.5$ K was $\sim 21$ T$^4$ suggesting that a relatively large $H_{c2}(0)$ value (on the order of $\sim 10^2$ T) for $T_c \sim 15$ K could be reasonable if the slope $|dH_{c2}(T)/dT)|_{T_c}$ of Bi$_{4-x}$Mn$_x$O$_3$S$_3$ was comparable to or even larger than that of the parent compound BiO$_3$S$_3$. On the other hand, in contrast to the studies of non-magnetic BiO$_3$S$_3$, the $H_{c2}(0)$ values of magnetic Bi$_{4-x}$Mn$_x$O$_3$S$_3$ could not be directly derived from the standard field-dependent resistive measurements due to the absence of $H$-dependent resistive transitions near $T_c \sim 15$ K and the fact that the WHH theory is only applicable to studies near $T_c$. Ultimately, better determinations...
The observation of both enhanced superconductivity and long-range ferromagnetism in the Mn-doped Bi$_4$O$_3$S$_3$ samples may be associated with the unique location and valences of the Mn-ions in the Bi$_4$O$_3$S$_3$ compound. First, Mn-ions may be preferentially located in the Bi$_2$O$_2$ spacers rather than in the BiS$_2$ layers so that severe lattice distortion from the large size differences between the Bi- and Mn-ions can be prevented in the superconducting BiS$_2$ layers. Additionally, XPS studies on Bi$_{1-x}$Mn$_x$O$_3$S$_3$ revealed that the valences of Mn-ions are found to be 3+ and 4+ (Fig. 3(a)). The substitution of Mn$^{4+}$ for Bi$^{3+}$ would result in excess electron doping and contribute to the electronic density of states at the Fermi level in the electron-type Bi$_4$O$_3$S$_3$ superconducting system, thus enhancing $T_c$.

IV. DISCUSSION

A. Possible physical origin for enhanced superconductivity and coexisting ferromagnetism in Bi$_{1-x}$Mn$_x$O$_3$S$_3$

The observation of both enhanced superconductivity and long-range ferromagnetism in the Mn-doped Bi$_4$O$_3$S$_3$ samples may be associated with the unique location and valences of the Mn-ions in the Bi$_4$O$_3$S$_3$ compound. First, Mn-ions may be preferentially located in the Bi$_2$O$_2$ spacers rather than in the BiS$_2$ layers so that severe lattice distortion from the large size differences between the Bi- and Mn-ions can be prevented in the superconducting BiS$_2$ layers. Additionally, XPS studies on Bi$_{1-x}$Mn$_x$O$_3$S$_3$ revealed that the valences of Mn-ions are found to be 3+ and 4+ (Fig. 3(a)). The substitution of Mn$^{4+}$ for Bi$^{3+}$ would result in excess electron doping and contribute to the electronic density of states at the Fermi level in the electron-type Bi$_4$O$_3$S$_3$ superconducting system, thus enhancing $T_c$.

The aforementioned conjecture of increased electronic carrier densities from Mn-doping to the Bi$_4$O$_3$S$_3$ compound has indeed been corroborated by our Hall effect measurements of both pure Bi$_4$O$_3$S$_3$ and Bi$_{1-x}$Mn$_x$O$_3$S$_3$ samples. Specifically, the Hall effect measurements were carried out at 300 K with an applied magnetic field $H = 0.483$ T and an applied current $I = 10$ mA, and the Hall resistivity for each sample was obtained by averaging readings from multiple measurements on different contact positions of the sample via the van der Pauw method. For the parent compound Bi$_4$O$_3$S$_3$, the normal-state Hall coefficient $R_H$ was found to be $(1.302 \pm 0.005) \times 10^{-4}$ m$^2$C$^{-1}$, which corresponded to a bulk carrier density of $n = (6.056 \pm 0.028) \times 10^{22}$ m$^{-3}$. In contrast, for Mn-doped samples Bi$_{1-x}$Mn$_x$O$_3$S$_3$ with $x = 0.125$, the normal-state Hall coefficient was found to be $R_H = (3.716 \pm 0.243) \times 10^{-5}$ m$^2$C$^{-1}$, which yielded a bulk carrier density $n = (1.688 \pm 0.120) \times 10^{23}$ m$^{-3}$, more than 2.5 times that of Bi$_4$O$_3$S$_3$.

It is also interesting to note that the correlation between enhanced superconductivity and increased electron carrier densities in the BiS$_2$-based superconductors
FIG. 8. (Color online) X-ray photoelectron spectroscopy (XPS) of Bi$_{4-x}$A$_x$O$_4$S$_3$ with A = Mn, Co, Ni and $x = 0.125$: (a) Analysis of the XPS data for the Mn-2$p_{3/2}$ and Mn-2$p_{1/2}$ binding energies of Bi$_3$S$_7$Mn$_{0.125}$O$_4$S$_3$, showing that the valences of Mn-ions were mixtures of Mn$^{4+}$ (primary) and Mn$^{3+}$ (secondary) which gave rise to excess electron transfer to the BiS$_2$ layers. Analysis of the XPS data of Bi$_3$S$_7$Ni$_{0.125}$O$_4$S$_3$, showing the valence of Ni being Ni$^{2+}$ (primary), metallic Ni and Ni$^{3+}$ (secondary). The presence of minor metallic peaks suggested that a small fraction of Ni was not fully doped into Bi$_3$O$_4$S$_3$. (c) Analysis of the XPS data of Bi$_3$S$_7$Co$_{0.125}$O$_4$S$_3$, showing the valences of Co-ions being metallic Co (primary) and Co$^{2+}$ (secondary) suggesting that Co was not fully doped into Bi$_4$O$_4$S$_3$, similar to the situation encountered in Ni-doped samples.

has also been observed in the La$_{1-x}$M$_x$OBi$_2$S$_2$ (M = Th, Hf, Zr, Ti) system$^{23}$ where substitutions of tetravalent Th$^{4+}$, Hf$^{4+}$, Zr$^{4+}$ and Ti$^{4+}$ ions for trivalent La$^{3+}$ could induce superconductivity with $T_c$ up to 2.85 K while substitutions of divalent Sr$^{2+}$ for La$^{3+}$ could not yield superconductivity.

In addition to the effect of contributing excess carrier densities in the superconducting BiS$_2$ layers, magnetic Mn-ions could give rise to long-range ferromagnetism in Bi$_{4-x}$Mn$_x$O$_4$S$_3$ without directly affecting the Cooper pairing within the BiS$_2$ layers at $T < T_K$ if they were confined within the Bi$_2$O$_2$ spacer layers and coupled via the RKKY interaction.$^{25-27}$ Furthermore, the significant energy separation between the localized 3$d$ orbitals responsible for magnetism and the Fermi level within the itinerant 6$p$ orbitals for superconductivity also provides a favorable condition for coexisting superconductivity and ferromagnetism in Bi$_{4-x}$Mn$_x$O$_4$S$_3$. In this context, we speculate that the observation of coexisting ferromagnetism and superconductivity in CeO$_{1-x}$F$_x$BiS$_2$ and Sr$_{0.5}$Ce$_{0.5}$FBiS$_2$ compounds$^{15-17}$ may also be attributed to the confinement of magnetic moments in the CeO$_{1-x}$F$_x$ and Sr$_{1-x}$Ce$_x$F spacer layers.

In principle, the location of Mn ions in Bi$_{4-x}$Mn$_x$O$_4$S$_3$ may be identified by applying the Rietveld method to analyze the x-ray diffraction spectra.$^{28}$ However, our attempts of using the Rietveld refinement could not conclude that Mn ions only substituted Bi ions in the Bi$_2$O$_2$ layers because of too many fitting parameters. Future x-ray or neutron scattering experiments on single crystalline materials would be the best approach to conclusively determine the position of the doped Mn-ions.

Our conjecture of Cooper-pairing preservation in the BiS$_2$ layers from the influence of adjacent ferromagnetic spacers is analogous to the findings in cuprate superconductivity, where substitutions of strong magnetic moments (such as Gd, Eu and Sm) in layers other than the CuO$_2$ planes do not result in noticeable degradation of superconductivity.$^{22,23}$ On the other hand, the significantly suppressed $T_{c,ρ}$ relative to $T_c$ in Bi$_{4-x}$Mn$_x$O$_4$S$_3$ is likely due to the weak-link nature and ferromagnetic domain-induced superconducting phase fluctuations in these polycrystalline samples.

Finally, we note that the large $H_{c2}(0)$ value estimated from our specific heat data also implies that the Bi$_{4-x}$Mn$_x$O$_4$S$_3$ system can support superconductivity under substantially large effective magnetic fields, whether the fields are from external sources or due to local magnetic moments. The coexistence of superconductivity and ferromagnetism could also result in stronger superconducting fluctuations and contribute to a larger upper critical field. This interplay of superconductivity and ferromagnetism on the magnitude of the upper critical field of Bi$_{4-x}$Mn$_x$O$_4$S$_3$ is an interesting issue worthy of further theoretical investigation.

B. Comparative studies of Bi$_{4-x}$Co$_x$O$_4$S$_3$ and Bi$_{4-x}$Ni$_x$O$_4$S$_3$

We have also investigated the effects of other 3$d$ transition-metal doping on Bi$_4$O$_4$S$_3$, and found that ferromagnetism also coexists with superconductivity for
Bi$_{1-x}$Co$_x$O$_4$S$_3$ and Bi$_{4-x}$Ni$_x$O$_4$S$_3$ with $x = 0.1$ and 0.125. As exemplified in Fig. 2(c), XRD studies indicated that the lattice constants of Bi$_{3.875}$Co$_{0.125}$O$_4$S$_3$ and Bi$_{3.875}$Ni$_{0.125}$O$_4$S$_3$ were all reduced relative to those of Bi$_3$O$_4$S$_3$, similar to the findings from Bi$_{4-x}$Mn$_x$O$_4$S$_3$ (Fig. 1(a)). The $T_c,p$ and $T_c,M$ values only exhibited small variations from those of the parent compound Bi$_4$O$_4$S$_3$, as shown in Fig. 2(a)-(d). On the other hand, the positive saturation magnetizations in the FC curves for both Bi$_{3.875}$Co$_{0.125}$O$_4$S$_3$ and Bi$_{3.875}$Ni$_{0.125}$O$_4$S$_3$ were smaller than that of Bi$_{3.875}$Mn$_{0.125}$O$_4$S$_3$ (Fig. 10), whereas the corresponding ZFC curves remain positive at all temperatures, in stark contrast to the strong diamagnetism developed in Bi$_{3.875}$Mn$_{0.125}$O$_4$S$_3$ at $T < 40$ K (Fig. 2). Moreover, no enhancement of superconductivity relative to the parent compound Bi$_4$O$_4$S$_3$ was found in either Bi$_{4-x}$Co$_x$O$_4$S$_3$ or Bi$_{4-x}$Ni$_x$O$_4$S$_3$ so that anomalies associated with superconductivity in the $M$-vs.-$H$ loops completely vanished at $T > T_c = 4.8$ K, as exemplified in Fig. 2(a)-(b) for Bi$_{3.875}$Co$_{0.125}$O$_4$S$_3$.

XPS studies of Bi$_{4-x}$Ni$_x$O$_4$S$_3$ and Bi$_{4-x}$Co$_x$O$_4$S$_3$ (Fig. 2(b)-(d)) further revealed that the valences of Ni ions were either 2+ or 3+ and that of Co ions was purely 2+, in contrast to the 3+ and 4+ valences of Mn ions in Bi$_{4-x}$Mn$_x$O$_4$S$_3$ (Fig. 2(a)). These comparisons suggest that the unique 4+ valence of Mn ions may play an important role in the enhanced superconductivity and ferromagnetism in Bi$_{4-x}$Mn$_x$O$_4$S$_3$ by contributing excess conducting electrons to the superconducting BiS$_2$ layers while retaining localized magnetic moments in the Bi$_2$O$_2$ spacer layers. The onset of diamagnetic signals at $T < \sim 40$ K in the ZFC magnetization curves of Bi$_{4-x}$Mn$_x$O$_4$S$_3$ (Fig. 2 and Fig. 10) further provides a tantalizing hint for reaching even higher-$T_c$ values in the BiS$_2$-based superconductors.

V. CONCLUSION

We have demonstrated in this work thermodynamic evidences for enhanced superconductivity and its coexistence with ferromagnetism in Mn-doped layered superconductors, Bi$_{4-x}$Mn$_x$O$_4$S$_3$ ($0.075 \leq x \leq 0.15$). Our studies suggest that the robustness of superconductivity against ferromagnetism in these BiS$_2$-based superconductors may be attributed to the layered structure and the significant energy separation between the localized 3d orbitals responsible for magnetism and the Fermi level within the 6p orbitals for superconductivity. In particular, Mn-doping induces an enhancement of $T_c$ from 4.5 K up to $\sim 15$ K, whereas comparable doping of Ni and Co reveals only coexistence of superconductivity and ferromagnetism without discernible enhancement in $T_c$ relative to Bi$_4$O$_4$S$_3$. We attribute the unique $T_c$ enhancement in Bi$_{4-x}$Mn$_x$O$_4$S$_3$ to the Mn$^{4+}$/Mn$^{3+}$ mixed valences that contribute excess electrons to the superconducting BiS$_2$ layers, which has been further corroborated by the Hall effect studies. These findings have therefore revealed new pathways to enhancing the $T_c$ of BiS$_2$-based layered superconductors. However, complete elucidation of the microscopic mechanism and the interplay between superconductivity and ferromagnetism in the BiS$_2$-based superconductors still awaits future development of single crystalline materials.

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FIG. 9. (Color online) Resistive and magnetic characterizations of Bi_{4-x}A_xO_4S_3 (A = Co, Ni, Mn and x = 0.125): (a) Comparison of the $\rho$-vs.-$T$ data up to $T = 150$ K for different 3d transition-metal substitutions in the Bi$_4$O$_4$S$_3$ system. (b) Comparison of the $\rho$-vs.-$T$ data at low temperatures (up to $T = 7.5$ K) for different 3d transition-metal substitutions. (c) Comparison of the low-temperature (up to $T = 7.5$ K) ZFC $M$-vs.-$T$ data for different 3d transition-metal substitutions. (d) Comparison of the $T_{c,\rho}$ and $T_{c,M}$ values for different 3d transition-metal substitutions in Bi$_4$O$_4$S$_3$. We note that the $T_{c,\rho}$ values exhibit anti-correlation with the lattice constants shown in the inset of Fig. 1(c).

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FIG. 10. (Color online) ZFC and FC $M$-vs.-$T$ data of Bi$_{4-x}$AxO$_4$S$_3$ (A = Co, Ni, Mn and x = 0.125): The ZFC $M$-vs.-$T$ curves for samples doped with Co and Ni always revealed positive magnetization except when $T < 4.5$ K, whereas their FC $M$-vs.-$T$ curves all exhibited strong increase in magnetization, suggesting the presence of long-range ferromagnetism. In contrast, only the ZFC $M$-vs.-$T$ curve for the Mn-doped sample Bi$_{3.875}$Mn$_{0.125}$O$_4$S$_3$ exhibited diamagnetism for $T < 40$ K whereas the FC $M$-vs.-$T$ curve also revealed strong enhancement of positive magnetization below 50 K, suggesting the appearance of long range ferromagnetism.

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