Physical properties of $A_xFe_{2-y}S_2$ ($A$=K, Rb and Cs) single crystals

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We successfully synthesized two new compounds Rb$_x$Fe$_{2-y}$S$_2$ and Cs$_x$Fe$_{2-y}$S$_2$ which were isostructural with K$_x$Fe$_{2-y}$Se$_2$ superconductor. We systematically investigated the resistivity, magnetism and thermoelectric power of $A_xFe_{2-y}S_2$ ($A$=K, Rb and Cs) single crystals. High temperature resistivity and magnetic measurements show anomalies above 500 K depending on $A$ which are similar to $A_xFe_{2-y}Se_2$. Discrepancy between ZFC and FC curves was observed in K$_x$Fe$_{2-y}S_2$ and Rb$_x$Fe$_{2-y}S_2$, while it disappears in Cs$_x$Fe$_{2-y}S_2$. Our results indicate the similar magnetism between $A_xFe_{2-y}S_2$ and $A_xFe_{2-y}Se_2$ at high temperature.

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The discovery of iron-based high temperature superconductors attracted much attention in these years and it provided a new family of materials to explore the mechanism of high-$T_c$ superconductivity besides cuprate superconductors. Among all the iron-based superconductors, the anti-PbO type FeSe$_2$ owning the simplest structure with the edge-sharing FeSe$_4$ tetrahedra formed FeSe layers stacking along the c-axis. FeSe$_x$ displays a lower $T_c$ of 8 K at ambient pressure and $T_c$ can reach 37 K (onset) under 4.5 GPa. The corresponding pressure dependent ratio of $T_c$ can reach as large as $dT_c/dP$ of ~9.1 K/GPa, which is the highest among all the Fe-base superconductors. Recently, by intercalating K, Rb, Cs and Tl between the FeSe layers, superconductivity has been enhanced to about 30 K without any external pressure in Fe-Se system. The $A_xFe_{2-y}S_2$ ($A$=K, Rb, Cs and Tl) superconductors are isostructural to 122 iron-pnictide superconductors owning the simplest structure with the edge-sharing FeSe$_4$ tetrahedra formed FeSe layers stacking along the c-axis. FeSe$_x$ displays a lower $T_c$ of 8 K at ambient pressure and $T_c$ can reach 37 K (onset) under 4.5 GPa. The corresponding pressure dependent ratio of $T_c$ can reach as large as $dT_c/dP$ of ~9.1 K/GPa, which is the highest among all the Fe-base superconductors. The fundamental differences between the superconducting samples $K_xFe_{2-y}Se_2$ and non-superconducting samples $K_yFe_{2-y}S_2$ is not clear and detailed physical properties of intercalated FeS samples need further investigation. In this paper, we successfully synthesized two new compounds Rb$_x$Fe$_{2-y}S_2$ and Cs$_x$Fe$_{2-y}S_2$ which were isostructural to $K_xFe_{2-y}S_2$. We systematically investigated the physical properties of $A_xFe_{2-y}S_2$ ($A$=K, Rb and Cs) single crystals. Resistivity and magnetic measurements show anomalies above 500 K depending on $A$. We attribute these anomalies to the structural and antiferromagnetic transitions compared to the isostructural superconducting $A_xFe_{2-y}Se_2$ ($A$=K, Rb and Cs) compounds. $K_xFe_{2-y}S_2$ shows semiconductor behavior at low temperature the same to the previous report. The resistivity of Rb$_x$Fe$_{2-y}S_2$ and Cs$_x$Fe$_{2-y}S_2$ shows broad humps which is similar to superconducting $A_xFe_{2-y}Se_2$ samples, but no superconducting transition was observed in these samples. Single crystals of $A_xFe_{2-y}S_2$ were characterized by powder X-ray diffraction (XRD), X-ray single crystal diffraction, Energy-dispersive X-ray spectroscopy (EDX), direct current (dc) magnetic susceptibility, electrical transport and thermoelectric power (TEP) measurements. Resistivity below 400 K was measured using the Quantum Design PPMS-9. The resistivity measurements above 400 K was carried out with an alternative current resistance bridge (LR700P) by using the a Type-K Chromel-Alumel thermocouples as thermometer in a home-built vacuum resistance oven. Magnetic susceptibility was measured using the Quantum Design SQUID-MPMS. A high-temperature oven was used in the SQUID-PPMS for magnetic susceptibility measurement above 400 K. Single crystals $A_xFe_{2-y}S_2$ were grown by Bridgeman method with the nominal composition $A$Fe:S = 0.8:2.2. Starting material FeS was obtained by reacting Fe powder with FeS powder at 1700°C for 4 hours. Alkali metals and FeS powder were sealed into two wall quartz tubes. The mixture was heated to 1050 °C in 4 hours and then kept at this temperature for 2 hours, and later slowly cooled down to 750 °C at a rate of 6 °C/hour. After that, the temperature was cooled down to room temperature by shutting down the furnace. Plate-like single crystals can be cleaved from the final products.

Figure 1 shows the X-ray single crystal diffraction and powder XRD after crushing the single crystals to powder for $A_xFe_{2-y}S_2$. Only (00l) diffraction peaks were
increasing of alkali ion radius from K to Cs. The A and 14.801 Å Cs perpendicularly to the plane of the single crystal. The A conducting samples A of K for x and Cs A x and Cs A respectively. The actual compositions A, Rb and Cs respectively, it is consistent with the increasing of alkali ion radius from K to Cs. The lattice constants of a-axis for KFe2−yS2, RbFe2−yS2 and CsFe2−yS2 were determined to be 3.772 Å, 3.789 Å and 3.824 Å respectively. The actual compositions of KFe2−yS2, RbFe2−yS2, CsFe2−yS2 were determined by EDX to be K0.68Fe1.70S2, Rb0.74Fe1.67S2 and Cs0.72Fe1.71S2 respectively.

Figure 2(a) shows the temperature dependence of the resistivity for AFe2−yS2. The magnetic susceptibilities show sharp drop above 500 K with decreasing the temperature for all the samples which indicates antiferromagnetic transition at high temperature in this kind of materials. At the temperature below 400 K, the susceptibilities nearly show no temperature dependence.

We compared the high temperature resistivity with the susceptibility above 400 K as shown in Fig. 3. We found the anomaly temperature determined by the resistivity (T_r) is slightly higher than the antiferromagnetic transition temperature (T_N). The detailed temperatures of T_r and T_N for AFe2−yS2 are listed in Table.
I. $T_r$ and $T_N$ increase with decreasing the lattice constant of c-axis. The temperature dependence of resitivity and susceptibility around the temperature of $T_N$ for K$_x$Fe$_{2-y}$Se$_2$ (a), Rb$_x$Fe$_{2-y}$Se$_2$ (b) and Cs$_x$Fe$_{2-y}$Se$_2$ (c).

![FIG. 3](image_url)

**FIG. 3**: (color online). The temperature dependence of resistivity and susceptibility around the temperature of $T_N$ for K$_x$Fe$_{2-y}$Se$_2$ (a), Rb$_x$Fe$_{2-y}$Se$_2$ (b) and Cs$_x$Fe$_{2-y}$Se$_2$ (c).

between $A_x$Fe$_{2-y}$S$_2$ and $A_x$Fe$_{2-y}$Se$_2$, we ascribe the sudden increase of resistivity to the structural transition arising from the Fe vacancy ordering. We can conclude that all the samples of $A_x$Fe$_{2-y}$Ch$_2$($A$=K, Rb and Cs, Ch=S,Se) exhibit the common features of antiferromagnetic and structural transition at high temperature. Although $A_x$Fe$_{2-y}$S$_2$ and $A_x$Fe$_{2-y}$Se$_2$ show the same physical properties in normal state, no superconductivity was found in $A_x$Fe$_{2-y}$S$_2$.

![FIG. 4](image_url)

**FIG. 4**: (color online). The temperature dependence of thermoelectric power of K$_x$Fe$_{2-y}$S$_2$ (a), Rb$_x$Fe$_{2-y}$S$_2$ and Cs$_x$Fe$_{2-y}$S$_2$ (b).

Figure 4(a) shows the temperature dependence of TEP for K$_x$Fe$_{2-y}$S$_2$. The TEP for K$_x$Fe$_{2-y}$S$_2$ exhibits large negative value at room temperature. With decreasing the temperature, the absolute value of TEP gradually decreases and became small negative value at low temperature which is similar to K$_x$Fe$_{2-y}$Se$_2$. Fig. 4(b) shows the temperature dependence of TEP for Rb$_x$Fe$_{2-y}$S$_2$ and Cs$_x$Fe$_{2-y}$S$_2$. The TEP for both the two samples shows negative value at room temperature. With decreasing the temperature, the absolute value of TEP for Rb$_x$Fe$_{2-y}$S$_2$ gradually decreases and TEP shows small positive value at low temperature which indicates the multiple-band electronic structure in Rb$_x$Fe$_{2-y}$S$_2$. For Cs$_x$Fe$_{2-y}$S$_2$, the absolute value of TEP decreases with decreasing the temperature and still exhibit negative at low temperature. The different temperature de-
Table I: The summary of the actual compositions determined by EDX analysis with errors within 5%, the a-axis lattice parameters and the c-axis lattice parameters, the abnormal temperature determined by the susceptibility (T_a) and resistivity (T_r) for all the crystals A_xFe_{2-y}S_2 (A = K, Rb, Cs).

| sample name | A: Fe: Se | a (Å) | c (Å) | T_a (K) | T_r (K) |
|-------------|-----------|-------|-------|---------|---------|
| K_xFe_{2-y}S_2 | 0.68: 1.70: 2 | 3.772 | 13.546 | 565 | 571 |
| Rb_xFe_{2-y}S_2 | 0.74: 1.67: 2 | 3.789 | 14.070 | 546 | 558 |
| Cs_xFe_{2-y}S_2 | 0.72: 1.71: 2 | 3.824 | 14.801 | 518 | 524 |

FIG. 5: (color online). ZFC and FC dc magnetic susceptibility with the field 1000 Oe applied within the ab plane for A_xFe_{2-y}S_2 at low temperature.

The antiferromagnetic transition seems not directly connected to the superconductivity in this system. Almost the same antiferromagnetic transition temperatures between superconducting samples and insulating samples of K_xFe_{2-y}Se_2 samples also prove this. The different resistivity behaviors at low temperature for these samples might be due to the phase separation in this system similar to K_xFe_{2-y}Se_2 samples. The metallic phase without superconductivity may coexists with the insulating phase in this system, so with the different composition of metallic phase and insulating phase may results in the different hump temperatures. The maximum resistivity of Rb_xFe_{2-y}S_2 and Cs_xFe_{2-y}S_2 is about one order larger than the normal state resistivity of superconducting A_xFe_{2-y}Se_2, even in K_xFe_{2-y}S_2 no metallic resistivity behavior was observed. It indicates that the proportion of metallic phase in A_xFe_{2-y}S_2 is smaller than that in A_xFe_{2-y}Se_2. TEP clearly indicate the multi-band electronic structure in this system and the electronic structure is strongly dependent on A and Fe content in the samples. Discrepancy between ZFC and FC curves at low temperature might be related to the A and Fe content, or to the different Fe arrangement. The origin for the appearance of such behavior in this system still needs to be investigated.

In conclusion, we had successfully synthesized two new compounds Rb_xFe_{2-y}S_2 and Cs_xFe_{2-y}S_2 which were isostructural with K_xFe_{2-y}Se_2. Resistivity and susceptibility anomalies were observed above 500 K for A_xFe_{2-y}S_2 single crystals which was similar to superconducting A_xFe_{2-y}Se_2 samples. TEP indicated the multi-band electronic structure which was common in iron-based superconductors. Discrepancy between ZFC and FC curves at low temperature was possibly related to the A and Fe content, or to the local environment of Fe ions.

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