Structure and physical properties of new layered iron oxychalcogenide BaFe$_2$OSe$_2$

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We have successfully synthesized a new layered iron oxychalcogenide BaFe$_2$OSe$_2$ single crystal. This compound is built up of Ba and Fe-Se(O) layers alternatively stacked along the c-axis. The Fe-Se(O) layers contain double chains of edge-shared Fe-Se(O) tetrahedra that propagate along the b-axis and are bridged by oxygen along the a-axis. Physical property measurements indicate that BaFe$_2$OSe$_2$ is a semiconductor without the Curie-Weiss behavior up to 350 K. There is a possible long range antiferromagnetic (AFM) transition at 240 K, corresponding to the peak in specific heat measurement and two glassy transitions at 115 K and 43 K. The magnetic entropy up to 300 K is much smaller than the expected value for Fe$^{2+}$ in tetrahedral crystal fields and Mössbauer spectrum indicates that long range magnetic order is unlikely at 294 K. Both results suggest that a short range magnetic correlations exist above the room temperature.

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I. INTRODUCTION

The discovery of layered iron oxypnictides (Ln(O,F)FeAs, Ln = rare earth elements, 1111-type) superconductors with $T_c$ up to 56 K$^1$ has stimulated great interest in mixed-anion materials. Mixed anions from the same row of the Mendeleev periodic table tend to randomly occupy the same crystallographic site (anion disorder) because of the relatively similar sizes. On the other hand, if the anions are from different rows (oxysulfide or oxyselenide compounds for example), the distinctive difference of anion sizes and ionic polarization might lead to ordered occupancy in the different crystallographic sites (anion order), often forming layered crystal structure.$^2$

The mixed-anion compounds have attracted some interest during the exploration of novel cuprate high temperature superconductors. Halooxocuprates are example where copper ions are coordinated with four oxygen ions, forming the CuO$_2$ sheet, whereas the halogen ion usually occupies a so-called apical site.$^3$ With proper electron or hole doping, halooxocuprates will become superconductors.$^4$ Besides superconductivity, mixed-anion materials also exhibit diverse physical properties. Copper oxychalcogenides LnCuOCh (Ch = S, Se, and Te), isostructural to 1111-type iron-based superconductors, are wide-gap p-type superconductors with transparent p-type conductivity, photoluminescence, and large third order optical nonlinearity.$^5$ Transition metal oxychalcogenides Ln$_2$O$_2$TM$_2$OCl$_2$ (TM = Mn, Fe, and Co) contain the layers built up by the edge-shared octahedral unit [TM$_2$OCl$_2$]$_{2-}$. These materials show strong electron-electron interactions (Mott insulators) on the two dimensional (2D) frustrated antiferromagnetic (AFM) checkerboard spin-lattice.$^4$–$^6$

The materials with [TM$_2$OCh$_2$]$_{2-}$ layers exhibit similar structural diversity to iron-based superconductors. This is understandable since new compounds can be obtained by simply replacing [FeAs] layers with [TM$_2$OCh$_2$]$_{2-}$ layers, such as LnOFeAs $\rightarrow$ Ln$_2$O$_2$TM$_2$OCl$_2$, AEFeAs (AE = alkali earth metals) $\rightarrow$ AE$_2$Fe$_2$TM$_2$OCh$_2$,$^7$–$^9$ and AEFeAs (A = alkali metals) $\rightarrow$ Na$_2$Fe$_2$OSe$_2$. Thus, it is of considerable interest to explore the structural derivatives of AEFe$_2$As$_2$ among the oxychalcogenide compounds.

Here, we report the detailed synthesis and physical properties of a new layered iron oxychalcogenide BaFe$_2$OSe$_2$ single crystal. Even though it has the same chemical formula and [TM$_2$OCh$_2$]$_{2-}$ layers, the structure is different from other iron oxychalcogenides with [TM$_2$OCh$_2$]$_{2-}$ layers. To the best of our knowledge, BaFe$_2$OSe$_2$ is the first layered iron oxychalcogenide with alkali earth metal. It shows a semiconducting behavior with possible successive spin-glass transitions at low temperature and short range antiferromagnetic order above the room temperature.

II. EXPERIMENT

Single crystals of BaFe$_2$OSe$_2$ were synthesized by a self-flux method. Ba rod, Fe powder, Fe$_2$O$_3$ powder and Se shot were used as starting materials. BaSe was pre-reacted by reacting Ba piece with Se shot at 800 °C for 12 hours. BaSe was mixed with other reagents and intimately ground together using an agate pestle and mortar. The ground powder was pressed into pellets, loaded in a alumina crucible and then sealed in quartz tubes with Ar under the pressure of 0.2 atmosphere. The quartz tubes were heated up to 600 °C in 10 h, kept at 600 °C for 12 h, ramped again to 1100 °C in 12 h, kept at 1100 °C for

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plate-like crystals with typical size $2 \times 2 \times 0.5 \text{ mm}^3$ can be grown. Except for heat-treatment, all of processes for sample preparation were performed in glove boxes filled with argon.

The crystal structure of BaFe$_2$OSe$_2$ crystal was identified by single crystal x-ray diffraction (XRD). The data were collected using the Bruker APEX2 software package$^{15}$ on a Bruker SMART APEX II single crystal x-ray diffractometer with graphite-monochromated Mo $K_{\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. Data processing and an empirical absorption correction were also applied using APEX2 software package. The structures were solved (direct methods) and refined by full-matrix least-squares procedures on $|F^2|$ using Bruker SHELXTL program software.$^{15}$ Obtained lattice parameters of BaFe$_2$OSe$_2$ are given in Table 1. Atomic coordinates, isotropic displacement parameters and selected interatomic bond distances and angles are listed in Table 2. Phase identity and purity were confirmed by powder X-ray diffraction carried out on a Rigaku miniflex X-ray machine with Cu $K_{\alpha}$ radiation ($\lambda = 1.5418$ Å). Structural refinements of powder BaFe$_2$OSe$_2$ sample was carried out by using Rietica software.$^{15}$

The average stoichiometry was determined by examination of multiple points using an energy-dispersive X-ray spectroscopy (EDX) in a JEOL JSM-6500 scanning electron microscope. The presence of oxygen was confirmed for BaFe$_2$OSe$_2$, but the exact amount could not be quantified because of experimental limitations. The average atomic ratios determined from EDX are Ba:Fe:Se $= 1.00(7):2.2(2):2.0(2)$, close to the ratio of stoichiometric BaFe$_2$OSe$_2$.

Mössbauer spectrum was taken in transmission mode with $^{57}$Co(Rh) source at 294 K and the parameters were obtained using WinNormos software.$^{22}$ Calibration of the spectrum was performed by laser and isomer shifts were given with respect to $\alpha$-Fe.

The X-ray absorption spectra of the Fe and Se K-edges were taken in transmission mode on powder samples of BaFe$_2$OSe$_3$ at the X19A beamline of the National Synchrotron Light Source. Standard procedure was used to extract the extended x-ray absorption fine-structure (EXAFS) from the absorption spectrum.$^{10}$

Electrical transport, heat capacity, and magnetization measurements were carried out in Quantum Design PPMS-9 and MPMS-XL5.

III. RESULTS AND DISCUSSION

Similar to K$_x$Fe$_{2-y}$Se$_2$ and BaFe$_2$S$_{3+y}$,$^{21,22}$ the structure of BaFe$_2$OSe$_3$ is built up by stacking the Ba cations and Fe-Se(O) layers alternatively along the $c$ axis (Fig. 1(a)). However, within the Fe-Se(O) layers, the connection of Fe-Se(O) tetrahedra in BaFe$_2$OSe$_2$ is distinctive different from those in K$_x$Fe$_{2-y}$Se$_2$ and BaFe$_2$S$_3$. In BaFe$_2$OSe$_2$, double chains of edge-shared Fe-Se(O) tetrahedra propagate along the Se atoms parallel to $b$-axis. The Fe-Se(O) double chains are bridged by oxygen along the $a$-axis (Fig. 1(a)). The bond distances of Fe-Se ($\sim 2.5$ Å) and Fe-O ($\sim 1.9$ Å) are very similar to distances in compounds where Fe is also in tetrahedral coordination (BaFe$_2$OSe$_3$: $d_{Fe-Se} \sim 2.4$ Å, Fe$_3$O$_4$: $d_{Fe-O} \sim 1.9$ Å). Because of different bond distances between Fe-Se and Fe-O, Fe atoms are located at the highly distorted tetrahedral environment when compared to other materials with pure Fe-Se tetrahedra. This distortion is also reflected in the significant deviation of bond angles from the value for the ideal tetrahedron (109.5$^\circ$). The bond angles range up to 130.38(10)$^\circ$ in BaFe$_2$OSe$_2$, much larger than the values in BaFe$_2$S$_3$ and K$_x$Fe$_{2-y}$Se$_2$. Moreover, the different connection of Fe-Se(O) leads to the larger nearest neighbor Fe-Fe distances ($d_{Fe-Fe} \sim 3.13$ Å) when compared to BaFe$_2$S$_3$ and K$_x$Fe$_{2-y}$Se$_2$. Using obtained Fe-Se and Fe-O bond lengths as shown in Table 2, the valence of Fe ions in BaFe$_2$OSe$_2$ can be calculated using the bond valence sum (BVS) formalism in which each bond with a distance $d_{ij}$ contributes a valence $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ with $R_{ij}$ as an empir-
tal XRD patterns of a BaFe$_2$, close to the values obtained from single crystal XRD.

˚largest balls show selenium atoms. smallest ball denote Fe, medium size ball shows oxygen whereas shows local coordination of Fe atoms in tetrahedra: central plane of the single crystal.

Based on the goodness of fit (0.9995) long range magnetic or-

tivity of Fe environment in BaFe$_2$OSe$_2$. Assuming similar recoil-free factors 8 % of fit area corresponds to approximately similar volume (crystallographic) phase fraction. Since such large impurity fraction would have been de-
tected in our X-ray experiments this might suggest that second doublet comes from undistorted FeSe$_4$ tetrahedra in BaFe$_2$OSe$_2$ with no oxygen bonds present. In other words, there might be 8% ionic disorder existing.

The local environments of Fe and Se such as bond distances are also analyzed by fitting the EXAFS data as shown in Fig. 3. For the Fe site, the nearest neighbors are one oxygen atom (d$_{Fe-O}$ = 1.8769(19) Å) and three Se atoms (1×Se(I) and 2×Se(II)) with two different distances (d$_{Fe-Se(II)}$ = 2.4706(6) Å and d$_{Fe-Se(II)}$ = 2.5540(4) Å). The next nearest neighbors are three Fe atoms (1×Fe(I) and 2×Fe(II)) with two different distances (d$_{Fe-Fe(II)}$ ~ 3.13 Å and d$_{Fe-Fe(II)}$ ~ 3.24 Å). On the other hand, for the Se site, the nearest neighbors are three Fe atoms with bond distances d$_{Fe-Se(I)}$ and d$_{Fe-Se(II)}$. The next nearest neighbors are three Ba atoms (2×Ba(I) and 1×Ba(II)) with two different distances (d$_{Ba-Se(II)}$ = 3.3541(3) Å and d$_{Ba-Se(II)}$ = 3.4008(4) Å). From the joint analysis of Fe and Se edges EXAFS data using a single bond distance for Fe-O, Fe-

![FIG. 2. Mössbauer spectrum of BaFe$_2$OSe$_2$ at T = 294 K. Inset shows local coordination of Fe atoms in tetrahedra: central smallest ball denote Fe, medium size ball shows oxygen whereas largest balls show selenium atoms.](image)

![FIG. 3. FT magnitudes of the EXAFS oscillations (symbols) for Fe K-edge (a) and Se K-edge (b). The model fits are shown as solid lines. The FTs are not corrected for the phase shifts and represent raw experimental data. Insets of (a) and (b) filtered EXAFS (symbols) with k-space model fits (solid line).](image)

| Chemical Formula | BaFe$_2$OSe$_2$ | Formula Mass (g/mol) | 422.94 |
|------------------|-----------------|----------------------|--------|
| Crystal System   | orthorhombic    | Space Group          | Pmmn (No. 59) |
| a (Å)            | 9.8518(7)       | b (Å)                | 4.1332(3) |
| c (Å)            | 6.7188(4)       | V (Å$^3$)            | 273.59(3) |
| Z                | 2               | Density (g/cm$^3$)   | 5.134 |
| R1/wR2 (F$_0$ > | 0.9995)         | Goodness-of-Fit      | 1.187 |

$^a$ R1 = |F$_0$|/|F$_c$|/|F$_0$|, $^b$ wR2 = |F$_0$| - |F$_c$|/|wF$_0$|.$^c$
TABLE II. Atomic Coordinates, Equivalent Isotropic Displacement Parameters, and Selected Bond Lengths and Angles for BaFe₂OSe₂.

| Atom | Wyckoff | x     | y     | z     | Ueq (Å²) |
|------|---------|-------|-------|-------|----------|
| Ba   | 2b      | 3/4   | 1/4   | 0.49047(4) | 0.00734(9) |
| Fe   | 4f      | 0.58580(5) | 3/4 | 0.87890(7) | 0.00915(11) |
| O    | 2a      | 3/4   | 3/4   | 0.7372(6) | 0.0089(5)  |
| Se   | 4f      | 0.45734(4) | 1/4 | 0.75887(5) | 0.00739(10) |

Interatomic Distances (Å)

|            |            |            |            |            |
|------------|------------|------------|------------|------------|
| Fe-Se      | 2.4706(6)  | Fe-Se      | 2.5540(4)  | Fe-O       | 1.8769(19) |
| Ba-Se      | 3.3541(3)  | Ba-Se      | 3.4008(4)  | Ba-O       | 2.649(2)   |
| Ba-Fe      | 3.7012(4)  |            |            |            |            |

Bond Angles (°)

|            |            |            |            |
|------------|------------|------------|------------|
| Se-Fe-Se   | 108.03(2)  | Se-Fe-Se   | 108.03(2)  | Se-Fe-O    | 130.38(10) |
| Se-Fe-O    | 76.950(15) | Se-Fe-Se   | 108.03(2)  | Fe-O        | 119.1(2)   |
| Fe-O-Fe    |            |            |            |            |

FIG. 4. Temperature dependence of the resistivity $\rho_{ab}(T)$ of the BaFe₂OSe₂ crystal with $H = 0$ (closed blue square) and 90 kOe (open red circle, H//c). Inset shows the fitting result of $\rho_{ab}(T)$ at zero field using thermal activation model. The red line is the fitted curve.

Se, Fe-Fe and Se-Ba, and by fitting the k range 2-14 Å⁻¹ for Fe K-edge and 2-12.9 Å⁻¹ for Se K-edge (insets of Fig. 3(a) and (b)), the fitted average bond lengths are $d_{Fe-O} = 1.87(2)$ Å, $d_{Fe-Se} = 2.500(8)$ Å, $d_{Fe-Fe} = 3.17(4)$ Å and $d_{Se-Ba} = 3.38(2)$ Å, which are consistent with the average bond distances derived from XRD fitting.

As shown in Fig. 4, the resistivity $\rho_{ab}(T)$ of BaFe₂OSe₂ crystal increases rapidly with decreasing temperature, suggesting that this compound is a semiconductor in measured temperature region. The semiconducting behavior of $\rho_{ab}(T)$ can be fitted using the thermal activation model $\rho_{ab}(T) = \rho_0 \exp(E_a/k_BT)$, where $\rho_0$ is a prefactor, $E_a$ is thermal activated energy and $k_B$ is the Boltzmann’s constant (inset in Fig. 4). The obtained $E_a$ is 0.360(2) eV and the room-temperature resistivity $\rho_{ab}(300K)$ is about 10 kΩ·cm. Both are much larger than in BaFe₂Se₃ (0.178 eV and 17 Ω·cm). The $E_a$ is also larger than in La₂O₂Fe₂OSe₂ where Fe has octahedral coordination with 4×Se and 2×O mixed anions. The large $\rho_{ab}(300K)$ and $E_a$ could be due to the shorter Fe-O bond in highly distorted structure which localizes electrons and increases the band gap. Since La₂O₂Fe₂OSe₂ is a Mott insulator with narrow 3d electronic bands due to strong correlation effects, it is of interest to study whether BaFe₂OSe₂ is normal band insulator or Mott insulator via theoretical calculations. The $\rho_{ab}(T)$ measured at $H = 90$ kOe indicates that there is no obvious magnetoresistance in BaFe₂OSe₂ (Fig. 4).

The Curie-Weiss temperature dependence of $\chi(T)$ is not observed in BaFe₂OSe₂ single crystals up to 350 K (Fig. 5(a)). On the other hand, Mössbauer fit indicate that long range magnetic order is absent at 294 K. It implies that short range magnetic interactions might be present already at the room temperature. There is a peak in the $d(\chi(T))/dT$ curve at $T_1 = 240$ K for H//ab and the values of susceptibility between ZFC and FC curves are nearly the same at this temperature. This peak corresponds to the AFM transition temperature $T_N = 240$ K, confirmed by specific heat measurements. Moreover, the decrease in $\chi(T)$ with temperature is more significant than $\chi_{ab}(T)$. It suggests that the easy-axis of magnetization direction could be in ab-plane. According to mean-field theory for collinear antiferromagnets, $\chi(T) \rightarrow 0$ along the easy-axis direction whereas it is nearly constant below $T_N$ for the field perpendicular to the easy-axis direction. With further decreasing temperature, there are two peaks in the $d(\chi(T))/dT$ curve at $T_2 = 115$ K and $T_3 = 43$ K, respectively (inset of Fig. 5(a)). The hysteresis between zero-field-cooling (ZFC) and field-cooling (FC) measurements implies that they are spin-glass-like transitions. The absence of hysteresis in isothermal $M(H)$ loops for $H \parallel ab$ (Fig. 4(b)) at $T = 1.8$ K and 250 K indicates that there are no ferromagnetic impurities.
Moreover, the slope of $M(H)$ increases with increasing temperature consistent with the AFM behavior observed in $\chi(T)$ curves (Fig. 5(b)).

As shown in Fig. 6, the specific heat $C_p$ of BaFe$_2$OSe$_2$ approaches the value of 3NR at high temperature ($T = 300$ K) assuming $N = 6$, where $N$ is the atomic number in the chemical formula and $R$ is the gas constant ($R = 8.314$ J mol$^{-1}$ K$^{-1}$). It confirms the atomic numbers of BaFe$_2$OSe$_2$ obtained from single crystal XRD fitting and consistent with the atomic ratio measured from EDX. On the other hand, at the low temperature, $C_p(T)$ curve can be fitted by a cubic term $\beta T^3$ (inset of Fig. 6) and the fitted value $\beta$ is $0.852(2)$ mJ mol$^{-1}$ K$^{-1}$. According to the formula $\Theta_D = (12\pi^4 N R / 5\beta)^{1/3}$, Debye temperature is estimated to be $\Theta_D = 239.1(2)$ K. The larger $\Theta_D$ when compared to BaFe$_2$Se$_3$ ($\Theta_D = 205(1)$ K) can be ascribed to the smaller atomic mass of oxygen than selenium.

There is a $\lambda$-type anomaly at $T_1 = 241.7$ K as shown in Fig. 6. The peak position is very close to the peak position ($T_I = 240$ K) at $d\chi(T)/dT$ curve (inset of Fig. 5(a)). It suggests that a long-range AFM ordering forms at this temperature. After substraction the phonon contribution ($C_{ph}$) fitted using a polynomial for the total specific heat, the magnetic contribution ($C_{mag}$) can be obtained. The magnetic entropy can be calculated using the integral

$$S_{mag}(T) = \int_0^T C_{mag}/T \, dt.$$ 

The derived $S_{mag}$ is $\sim 1.83$ J/mol-K when $T$ is up to 300 K (Fig. 6), which is much smaller than expected values $R\ln(2S+1)$ for Fe$^{2+}$ ions with low spin state ($\sim 20\%$ Rhn3) and with high spin state ($\sim 13.7\%$ Rhn5) in tetrahedral crystal fields. It is even less than Rhn2 for S=1/2 ($\sim 31.8\%$ Rhn2), suggesting that there is short range magnetic order at higher temperature which partially releases the magnetic entropy before any long range magnetic transition, consistent with the Mössbauer spectrum and magnetization measurement results. On the other hand, there is no peaks appear at $T_3 = 115$ K and $T_4 = 43$ K, confirming the glassy magnetic behaviors at those temperatures.

### IV. CONCLUSION

In summary, we report a discovery of a new layered iron oxychalcogenide BaFe$_2$OSe$_2$. The crystal structure features double chains of edge-shared Fe-Se(O) tetrahedra that propagate along the $b$-axis. The Fe-Se(O) double chains are bridged by oxygen along the $a$-axis. BaFe$_2$OSe$_2$ single crystals are magnetic semiconductors with a possible long range AFM transition at 240 K and two glassy transitions at 115 K and 43 K. The magnetic entropy up to 300 K is much smaller than expected for Fe$^{2+}$ in tetrahedral crystal fields, suggesting the existence of short range AFM correlation above room temperature. Because of the interesting structure and connectivity among the iron atoms, it is of interest to investigate the mechanism of magnetic ground state by theoretical calculations and by neutron scattering experiments. Moreover, doping effects on physical properties should further reveal similarities and differences with supercon-
ducting iron selenide compounds.

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