(CaO)(FeSe): A Layered Wide Gap Oxychalcogenide Semiconductor

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ABSTRACT: A new iron-oxychalcogenide (CaO)(FeSe) was obtained which crystallizes in the orthorhombic space group Pnma (No. 62) with a = 5.9180(12) Å, b = 3.8802(8) Å, c = 13.193(3) Å. The unique structure of (CaO)(FeSe) is built up of a quasi-two-dimensional network of corrugated infinite layers of corner-shared FeSeO₄ tetrahedra that extend in the ab-plane. The corrugated layers composed of corner-shared FeSeO₄ tetrahedra stack along the c-axis with Ca⁺ cations sandwiched between the layers. Optical spectroscopy and resistivity measurements reveal semiconducting behavior with an indirect optical band gap of around 1.8 eV and an activation energy of 0.19(1) eV. Electronic band structure calculations at the density function level predict a magnetic configuration as ground state and confirm the presence of an indirect wide gap in (CaO)(FeSe).

INTRODUCTION

The mixed anion systems such as oxynitrides and oxychalcogenides have shown fascinating properties highlighted by the discovery of iron-based superconductors with Tc up to 58 K.1,2 These systems usually adopt layered structures allowing segregation of the two anions, owing to their different chemical nature.3 In the iron-oxynitride superconductors LnFe₂O₅ (Ln = rare earth),4 Sr₂CO₃Fe₃O₇,5 and SrₓVOₓFeAs₆ FeX (X = pnictide) layers of antifluorite-like edge-shared FeX₄ tetrahedra are responsible for the superconductivity while oxide spacer layers act as charge reservoirs which can be doped. Since β-FeSe (under high pressure),9a,9b KFe₂Se₂12–14 and FeSe with molecular interlayers9b,9c were observed to be superconducting above 30 K, the exploration of new iron-oxychalcogenide compounds has intensified. In the past several years, a series of new iron-oxynitridochalcogenides including NaFe₂Se₂O10,11 A⁺FeₓQₓOₓ (A⁺ = Sr, Ba, Q = S, Se)12–14, β-La₂O₅M₂Se₂ (M = Mn, Fe),13 Ce₂O₅FeSe₂14 and (BaF)₂Fe₂O₅15 (Q = S, Se)16 were reported. These materials along with the previously reported LnOₓFeₓO₃Seₓ17–18 and A⁺FeₓFeₓO₃Seₓ19 (A⁺ = alkaline earth) are not superconductors. Coincidentally they do not contain isostuctural FeSe layers of antifluorite-like edge-shared FeSe₄ tetrahedra. In contrast the recently reported (Liₓ,xFex)OHFeSeₓ has a coexistence of superconductivity at 42 K and antiferromagnetism at 8.6 K,20,21 and it consists of FeSe₄ conductive layers providing superconductivity and (Liₓ,xFex)OH spacer layers in which at the shared Li/Fe site the observed antiferromagnetic ordering possibly happens.

In an effort to synthesize a new analogue containing FeSe layers and CaO spacer layers for a new iron-based superconductor which was also aimed by other groups,22 we discovered the new compound (CaO)(FeSe) which crystallizes in the orthorhombic space group Pnma (No. 62) with a = 5.9180(12) Å, b = 3.8802(8) Å, c = 13.193(3) Å. (CaO)(FeSe) adopts a new type of layered structure that remarkably features O²⁻ and S²⁻ anions in the same chain. (CaO)(FeSe) consists of corrugated slabs of corner-shared FeSeO₄ tetrahedra that extend along the ab-plane and stack along the c-axis with Ca⁺ cations sandwiched between the FeSeO₄ slabs. This new material is a wide band gap semiconductor with an indirect optical gap of around 1.8 eV.

EXPERIMENTAL SECTION

Sample Preparation. Single-crystalline (CaO)(FeSe) was grown from the melt. Our initial target was to prepare CaFe₂Se₂O with the following procedure: Precursor FeSe was firstly synthesized by direct combination of powdered Fe (Alfa Aesar, 99.9+% metals basis) and Se (Alfa Aesar, 99.999% metals basis). Starting materials of CaO powders (Sigma Aldrich, 99.9% trace metals basis) and the pre-reacted FeSe with the molar ratio of 1:2 and total mass of around 3 g were mixed and placed in an alumina crucible. All handling was performed in a glove box under Argon atmosphere (both H₂ and O₂ are limited below 0.1 ppm). The alumina crucible was jacketed by an evacuated silica tube. The tube was heated to 1000 °C in a box furnace and kept at 1000 °C for 10 hours. A slow-cooling process from 1000 °C to 700 °C was carried out during 60 hours. From the powder X-ray diffraction data, we found the resultant product consisted of CaSe, FeSe, FeO, and an unindexed phase. With the help of an optical microscope, we found some red transparent crystals covered by black melt in the product. A hand-picked crystal isolated from the black matrix is shown Figure 1(a). These red transparent crystals were finally determined as (CaO)(FeSe)
by single-crystal X-ray diffraction. After the stoichiometry of the new quaternary compound was elucidated, we tried a more rational synthesis of (CaO)(FeSe) by direct combination of a stoichiometric mixture of CaO and FeSe. The heating procedure was the same as above. However, the product was impure and consisted of CaSe, FeSe, CaFeO, CaFe2O4, and (CaO)(FeSe). The impure nature of the samples and the low yield of (CaO)(FeSe) phase made bulk measurements such as magnetic susceptibility and heat capacity impossible.

**Scanning Electron Microscopy.** Elemental analysis of (CaO)(FeSe) crystal was performed on a Hitachi S-4700-II Scanning Electron Microscope with Energy Dispersive Spectroscopy (EDS) detector equipped. Electron micrograph in the inset of Figure 1(b) shows the plate-like crystal habit of a single (CaO)(FeSe) crystal. Typical crystal dimensions were around 150 × 150 × 5 μm.3. Semiquantitative analysis by EDS indicated the crystal consisted of Ca, Fe, Se, and O, as shown in Figure 1(b), with an average composition of Ca1.22(2)Fe1.23(3)Se1.24(4)O1.91(2).

**Optical Spectroscopy.** Single-crystal absorption spectrum was obtained on a Hitachi U-6000 Microscopic FT spectrophotometer mounted on an Olympus BH2-UMA microscope. Crystal lying on a glass slide was positioned over the light source and the transmitted light was detected from above. The background signal of the glass slide was subtracted from the collected intensity.

**Table 1. Single Crystal Data and Structure Refinement for (CaO)(FeSe) Collected at Room Temperature.**

| Parameter | Value |
|-----------|-------|
| Empirical formula | (CaO)(FeSe) |
| Formula weight | 190.89 |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pnma |
| Unit cell dimensions | a = 5.980(1) Å, b = 9.00° |
| | b = 3.8802(1) Å, β = 90.00° |
| | c = 13.103(1) Å, γ = 90.00° |
| Volume | 302.95(1) Å³ |
| Z | 4 |
| Density (calculated) | 4.185 g/cm³ |
| Absorption coefficient | 18.38 mm⁻¹ |
| F(000) | 352 |
| Crystal size | 0.15 x 0.1 x 0.005 mm³ |
| θ range for data collection | 3.77 to 25.46° |
| Index ranges | -7 ≤ h ≤ 7, -4 ≤ k ≤ 4, -15 ≤ l ≤ 15 |
| Reflections collected | 1563 |
| Independent reflections | 315 [Rint = 0.0303] |
| Completeness to θ = 24.98° | 96% |
| Refinement method | Full-matrix least-squares on F² |
| Data / restraints / parameters | 315 / 0 / 25 |
| Goodness-of-fit | 1.143 |
| Final R indices [>2σ(I)] | Rint = 0.0447, wRint = 0.1096 |
| R indices [all data] | Rall = 0.0531, wRall = 0.1133 |
| Largest diff. peak and hole | 3.338 and -1.140 e-Å³ |

| Atom | x | y | z | Ueq |
|------|---|---|---|-----|
| Se   | 2430(2) | 2500 | 9040(1) | 9(1) |
| Fe   | 1125(2) | 2500 | 2920(2) | 13(1) |
| Ca   | 2484(3) | 2500 | 5806(2) | 9(1) |
| O    | 2919(13) | 2500 | 1745(6) | 11(2) |
**RESULT S AND DISCUSSION**

**Crystal Structure.** The layered structure of (CaO)(FeSe) projected onto the ac-plane is depicted in Figure 2(a). The structure is built up of a quasi-two-dimensional network of corrugated layers of corner-shared FeSeO₄ tetrahedra along ab-plane, as shown in Figure 2(b). Ca ions are sandwiched between the FeSeO₄ infinite layers which stack along the c-axis to form the (CaO)(FeSe) structure. The iron oxycarbotonide tetrahedra are perfectly ordered with O⁺ and Se⁻ occupying their own sites (Wyckoff position 4c). The connectivity of the corner-shared FeSeO₄ tetrahedra through the O/Se anions is directional with leverotatory and dextrorotatory Fe-O-Fe bridges alternatively replicating along the a-axis and with Fe-Se-Fe bridges infinitely replicating along the b-axis. Ca⁺ cations connect with O⁺ anions and form zig-zag (Ca-O)₈ chains along the b-axis. The unique feature of the (CaO)(FeSe) structure is that unlike most of other mixed anion systems which have the two types of anions segregated in different layers, (CaO)(FeSe) combines O⁺ and Se⁻ anions in the same layer. This structure is somewhat like that of AFe₂O₃ (A = Sr, Ba, Q = S, Se)₉⁻²² which also contain the structure fragment of Fe-O-Fe bridge leverotatory-and-dextrorotatory-alternatively flipping. In AFe₂O₃ (A = Sr, Ba, Q = S, Se)₉⁻²² the Fe-O-Fe bridges are glued by Se⁻ anions. Differently, in (CaO)(FeSe) the Fe-O-Fe bridges connect with each other by sharing Fe⁺ cations. The crystallographic data, selected bond distances, and bond angles for (CaO)(FeSe) are listed in Tables 1-4.

**Table 3. Anisotropic Displacement Parameters (Å²×10⁶) for (CaO)(FeSe) at Room Temperature.**

| Atom | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|------|-----|-----|-----|-----|-----|-----|
| Se   | 7(1) | 8(1) | 12(1) | 0   | 1(1) | 0   |
| Fe   | 12(1) | 15(1) | 13(1) | 0   | 4(1) | 0   |
| Ca   | 9(2) | 7(2) | 11(2) | 0   | 1(1) | 0   |
| O    | 12(3) | 11(4) | 11(4) | 0   | 1(3) | 0   |

*U_{ij} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

**Resistivity.** Temperature-dependent resistivity measurement was done on a Quantum Design physical property measurement system (PPMS). Considering the small dimensions of the crystal and the wide optical gap, we performed the resistivity measurement in two probe geometry in an arbitrary direction in the ab-plane using 14 µm gold wire and silver paste for making the electrical contacts.

**Band Structure Calculations.** The electronic band structure calculations have been carried out by using the full potential linearized augmented plane wave method as implemented in WIEN2k package. Local spin density approximation (LSDA) for the exchange-correlation potential has been used here. A 9x13x4 k-point mesh is used for the Brillouin zone integral. The self-consistent calculations are considered to be converged when the difference in the total energy of the crystal does not exceed 0.1 mRy and that in the total electronic charge does not exceed 0.1 e⁻ electronic charge at consecutive steps.

**Table 4. Bond Lengths [Å] and Bond Angles [°] for (CaO)(FeSe) at Room Temperature.**

| Atom-Atom | Bond Length (Å) | Bond Angle (°) |
|-----------|-----------------|----------------|
| Fe-O      | 1.888(8)        |                |
| Fe-O      | 1.945(8)        |                |
| Fe-Se(x2) | 2.5776(14)      |                |
| Ca-O(x2)  | 2.314(5)        |                |
| Ca-Se     | 2.934(2)        |                |
| Ca-Se     | 2.998(2)        |                |
| Ca-Se(x2) | 3.032(2)        |                |

*The anisotropic displacement factor exponent takes the form: -2π²h^2*a^2U₁₁ + ... + 2hka*b^2U₁₃*. There is only one crystallographically independent site for each atom in the asymmetric unit cell. Each Fe⁺⁺ cation is tetrahedrally coordinated by two O⁻⁺ and two Se⁻ anions while each Ca⁺⁺ cation is octahedrally coordinated by two O⁻⁺ and four Se⁻ anions, as shown in Figure 3(a) and 3(b). All interatomic bond lengths are within normal range, Table 4. Along the a-axis, Fe⁺⁺ cations and O⁻⁺ anions form a helical structure with alternating short (1.888(8) Å) and long (1.945(8) Å) bond lengths, Figure 3(c). In the helical [FeO₆]₁⁻ chains the distance of two most neighbored Fe atoms is 3.178(10) Å while that distance between the neighbor [FeO₆]₁⁻ chains is 3.8802(8) Å which are relatively short and expected to give strong Fe–Fe interactions. In contrast, the distance of two most neighbored Fe atoms between the neighbor FeSeO₃ layers is 5.9504(25) Å which could lead to a weak magnetic coupling between the layers. The FeSeO₃ tetrahedra and CaSeO₃ octahedra are distorted because of the different chemical nature of Se⁻ and O⁻⁺ anions. In the FeSeO₃ tetrahedra and the CaSeO₃ octahedra, anion-cation-anion bond angles are greatly different from each other. For example, in the FeSeO₃ tetrahedra O-Fe-O bond angle of 137.0(3)° is much larger than Se-Fe-Se angle of 97.65(9)° and both of them are far from the ideal angle of 109.5° for a regular tetrahedron.
Figure 2. (a) Perspective view of the layered structure of (CaO)(FeSe) along crystallographic b-axis. (b) Bond/stick model for (CaO)(FeSe).

Figure 3. (a) Coordination environment of Fe. (b) Coordination environment of Ca. (c) [Fe-O]₁₈₁ infinite chain viewed along the a-axis, Fe²⁺ cations and O²⁻ anions form a helical structure with alternating short and long Fe-O bond lengths.

**Optical Absorption.** Based on the charge balanced formula of Ca²⁺Fe²⁺Se²⁻O⁻ the compound is valence precise and is expected to be a semiconductor. Single-crystal absorption spectrum collected for (CaO)(FeSe) at room temperature reveal a broad band gap transition between 1.8 eV and 2.3 eV, Figure 4. For a direct optical transition the square of absorbance (a) is expected to vary linearly with energy hω as $a = (hω - E_D)^{1/2}$ where $E_D$ is the direct optical band gap. For an indirect transition the square root of a is expected to vary linearly with energy as $a = (hω - E_{Dg})^{1/2}$ where $E_{Dg}$ is the indirect band gap energy. Since the band gap of (CaO)(FeSe) is predicted in the following subsection to be indirect we plotted the square root of absorbance data as a function of energy (inset of Figure 4) and extracted an indirect band gap value of 1.83(2) eV. This wide energy gap is consistent with the red color of the crystals.

**Resistivity.** Temperature dependence of resistivity for a single crystal sample of (CaO)(FeSe) confirmed the semiconducting nature of the compound. The resistivity is around 35kΩ·cm at room temperature and increases gradually with falling temperature, Figure 5(a). Furthermore, above 256 K the temperature dependence of resistivity strictly obeys thermally activated behavior as $\rho = \rho_0 \exp(E_g/k_BT)$ where $\rho_0$ refers to a prefactor and $k_B$ is the Boltzmann’s constant, as
shown in Figure 5(b). Within this fitting process, the activation energy $E_a$ was extracted to be $0.19(1)$ eV. The activation energy is much smaller than the experimental band gap indicating the presence of mid-gap levels (likely to be the partially filled $d$ levels of high spin Fe$^{2+}$) which can thermally donate electrons to conduction band or accept electrons from the valence band.

The existence of 3D-VRH behavior in other layered transition metal compounds has been reported, which somehow indicates the strong correlation between layers. The variation of the dominant conduction mechanism with temperature can be explained with a model of two kinds of parallel conductive channels. When the temperature is high enough, electrons are activated across the barriers between the mid-gap energy levels and conduction bands or between valence bands and the mid-gap energy levels. As the temperature falls, the thermally activated electrons decay rapidly, and at low temperatures electrons or holes choose to move through localized Fe$^{2+}$ sites with longer distance but closer energy by a tunneling process stimulated by phonons.

**Figure 5.** (a) Resistivity as a function of temperature for a (CaO)(FeSe) single crystal. The experimental data obey thermal activation behavior at high temperatures and 3D variable range hopping behavior at low temperatures, respectively. (b) Arrhenius plot $\ln\rho$ vs $1000/T$ showing linear behavior between 256 K and 300 K. (c) Arrhenius plot $\ln\rho$ vs $T^{-\frac{1}{4}}$ showing linearity with $T$ less than 256 K.

When $1000/T$ is more than $3.9$ K$^{-1}$ ($T < 256$ K), the $\ln\rho$ vs $1/T$ curve begins to deviate from the original linearity. Initially we attempted to attribute this deviation to a smaller activation energy $E_a$ at lower temperatures, however, below 256 K the $\ln\rho$ vs $1000/T$ curve does not obey strict linearity. Instead, three-dimensional variable range hopping (3D-VRH) can better describe the resistivity behavior at low temperatures. We can see a new linear behavior in $\ln\rho$ vs $T^{-\frac{1}{4}}$ curve, Figure 5(c), which indicates below 256 K the 3D-VRH behavior as $\rho = \rho_0\exp(T/F)^{\frac{1}{4}}$ is obeyed, here $\rho_0$ and $T_0$ refer to prefactors.

**Band Structure Calculations.** In the structure of (CaO)(FeSe), the Fe sublattice can be considered two staggered distorted square nets, as shown in Figure 6(a). Fe1, Fe2, Fe3, Fe4 are labeled for the representation analysis of magnetic configurations. To search for the magnetic ground state configuration, we considered five AFM configurations besides the FM states as follows (Figure 6(b)): AFM-1 (Fe1 and Fe2, Fe3 and Fe4 couple ferromagnetically while Fe1 and Fe3 have opposite spin orientation, and neighbor [Fe-O]$_m$ chains in one layer couple ferromagnetically), AFM-2 (Fe1 and Fe3, Fe2 and Fe4 couple ferromagnetically while Fe1 and Fe2 have opposite spin orientation, and neighbor [Fe-O]$_m$ chains in one layer couple ferromagnetically), AFM-3 (Fe1 and Fe4, Fe2 and Fe3 couple ferromagnetically while Fe1 and Fe2 have opposite spin orientation, and neighbor [Fe-O]$_m$ chains in one layer couple ferromagnetically), AFM-4 (Fe1, Fe2, Fe3 and Fe4 couple ferromagnetically while neighbor [Fe-O]$_m$ chains in one layer couple antiferromagnetically) and AFM-5 (Fe1 and Fe3, Fe2 and Fe4 couple ferromagnetically while Fe1 and Fe2 have opposite spin orientation, and neighbor [Fe-O]$_m$ chains in one layer couple antiferromagnetically).

The LSDA calculation predicts that the AFM-2 state is the ground state, and the simulated $3.0 \mu_B$ magnetic moment mainly locates at the Fe site. As we can see from Table 5, the total energy of the AFM-3 state is only $20$ meV higher than the ground state which indicates that the magnetic coupling between the two layers is small, while the total energy of other configurations are about $0.2$ to $0.7$ eV higher than the ground state.
The calculations. It is well known that the electronic correlations are important in 3d orbitals, so we utilized an LSDA+U (U = 4 eV) scheme, which is adequate for the magnetically ordered insulating ground states. As with the LSDA calculations, the LSDA+U also predicts AFM-2 as the ground state, with an obtained magnetic moment of -3.3 μ₅B similar to the LSDA calculations.

The band structures of (CaO)(FeSe) from the LSDA+U calculations are presented in Figure 7 and the density of states in Figure 8. The band structures show (CaO)(FeSe) is an insulator with an indirect gap of about 1.55 eV, consistent with the experimental results of 1.8 eV. The energy range, -3.0 to 0.0 eV is dominated by Fe 3d states. The 12 bands located from -6.0 to -4.0 eV basically come from O 2p states, while the 12 Se 4p states distribute from -4.0 to -1.0 eV. All these indicate strong hybridization between Fe 3d states and Se 4p states. The Ca 4s states are located about 3.0 to 5.0 eV higher than the Fermi level.

Table 5. The Total Energy [meV] of Six Magnetic Configurations Calculated by Different Scheme, Compared with the Ground State.

|       | FM  | AFM-1 | AFM-2 | AFM-3 | AFM-4 | AFM-5 |
|-------|-----|-------|-------|-------|-------|-------|
| LSDA  | 522 | 516   | 0     | 20    | 742   | 244   |
| LSDA+U | 355 | 341   | 0     | 5     | 364   | 24    |

It is well known that the electronic correlations are important in 3d orbitals, so we utilized an LSDA+U (U = 4 eV) scheme, which is adequate for the magnetically ordered insulating ground states. As with the LSDA calculations, the LSDA+U also predicts AFM-2 as the ground state, with an obtained magnetic moment of -3.3 μ₅B similar to the LSDA calculations.
CONCLUDING REMARKS

We have successfully prepared a new iron-oxychalcogenide (CaO)(FeSe) which adopts a new structure type. The structure of (CaO)(FeSe) is unique with a combination of O²⁻ and Se²⁻ anions in the same FeSe₂O₄ layers. The structure is different from that of CaOFeSe₁₋ₓ₋₀.₄ (CaOFeS adopts a CaOZnS-type hexagonal structure) and our phase diagram studies of BaO-FeSe and SrO-FeSe only yielded BaFe₅Se₄O₉₋ₓ and SrFe₂Se₂Oₓ respectively. Therefore, the structure of (CaO)(FeSe) is stable for a restricted range of chalcogen and alkali-earth-metal elements.

ASSOCIATED CONTENT

Supporting Information
X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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