Synthesis, structure and physical properties of the new layered oxyselenides Bi$_2$LnO$_4$Cu$_2$Se$_2$ (Ln = rare earth)

Shugang Tan$^1$, Chenhao Gao$^1$, Cao Wang$^1$, Qiang Jing$^1$, Tong Zhou$^1$, Guangchao Yin$^1$, Meiling Sun$^1$, Fei Xing$^1$, Rui Cao$^2$ and Yuping Sun$^1$

$^1$School of Physics and Optoelectronic Engineering, and $^2$Office of International Cooperation and Exchange, Shandong University of Technology, Zibo 255000, People’s Republic of China

We have synthesized a new series of layered oxyselenides Bi$_2$LnO$_4$Cu$_2$Se$_2$ (Ln=Nd, Sm, Eu, Dy, Er, Yb). Their crystal structures and physical properties were studied through X-ray diffraction, electric transport measurements, bulk magnetization and first-principle calculation. All these compounds have a tetragonal structure with space group I4/mmm. They exhibit hole-type metallic behaviours which is also verified by the DFT calculation. The new Bi$_2$LnO$_4$-type block in these compounds may give people some enlightenment in synthesizing new iron-based superconductors or other layered compounds.

1. Introduction

Since the discovery of superconductivity, people have been trying to find new superconductors with application values. Compounds with layered structure have always attracted people’s attention because of their rich properties. Especially in recent years, many layered structural compounds have been found to exhibit superconductivity, such as cuprates superconductors [1], iron-based superconductors [2] and BiS$_2$-based superconductors [3]. It has become one of the most important ways to search for new superconductors by exploring novel layered structural compounds.

Oxychalcogenides tend to adopt layered structure, due to the different sizes and coordination requirements of the oxide and the heavier chalcogenide anions [4]. Oxychalcogenides have been extensively studied because of their novel electronic or magnetic properties and intriguing structure features. Generally,
TMCh-based (TM = Cu, Ag; Ch = S, Se, Te) oxychalcogenides dominated the known chemistry of oxychalcogenides, which possess very diverse and interesting structures and exhibit useful physical and chemical properties [4–9]. LnOTMCh (Ln = lanthanide) is a typical class of layered oxychalcogenides. The formulation as LaOCuS emphasizes the occurrence of two fairly distinct layer types, formally [LaO]+ and [CuS]2+. The analogue BiCuSeO has attracted much attention in the thermoelectric field [10–13]. Another important type is represented by the Sr2MgCu2Ch2, the structure of which was first described for the oxide antimonide Sr2Mn3Sb2O8 [14–20]. These layered types have great flexibility and are each merely the most common members of the structural homologous series. In 2008, the discovery of Fe-based superconductor opens a new chapter in the research of high-temperature superconductivity. The common feature of iron-based superconductors is that they have Fe2Pn2 antifluorite layer. Many of the compounds with CuSe layers have analogues with FeAs layers, and there could be iron arsenides with this structure. In 2002, Evans et al. reported a new family of layered oxyselenide Bi2LnO4Cu2Se2, and five compounds were synthesized (Ln = Y, Gd, Sm, Nd, La) [21]. However, the physical properties of this series of oxyselenides are still unstudied. Recently, we studied the physical and electrical properties of Bi2YO4Cu2Se2, which exhibits quasi-two-dimensional metallic behaviour [22]. More compounds are needed to enrich this class of materials.

In this work, we report the synthesis, structure and physical properties several new compounds of the series Bi2LnO4Cu2Se2 (Ln = Sm, Nd, Eu, Dy, Er, Yb), which could give people some enlightenment in synthesizing new iron-based superconductors or other layered compounds.

2. Experimental details

Bi2LnO4Cu2Se2 sample was prepared by reacting a stoichiometric mixture of Bi2O3, Ln2O3, Bi, Cu and Se. The chemical equation can be written as

\[5\text{Bi}_2\text{O}_3 + 3\text{Ln}_2\text{O}_3 + 2\text{Bi} + 12\text{Cu} + 12\text{Se} \rightarrow 6\text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2.\]

The raw materials were mixed and ground thoroughly in an agate pestle and mortar, and then the mixture was pressed into pellets under 12 MPa. The pellets were placed into dried alumina crucibles and sealed under vacuum (less than 10^{-4} Pa) in the silica tubes which had been baked in a dry box for 1–2 h at 150°C. The ampoules were heated to 830°C with 1°C min^{-1} and maintained at this temperature for 24 h. Finally, the furnace was shut down and cooled to room temperature naturally. The obtained samples were reground, pelletized and heated for another 24 h at 830°C followed by furnace cooling. The X-ray powder diffraction patterns were recorded at room temperature on a Panalytical diffractometer (X’Pert PRO MRD) with Cu Kα radiation (40 kV, 40 mA) and a graphite monochromator in a reflection mode (2θ = 10–90°, step = 0.016°, scan speed = 5 s per step). Structural refinement of the samples was carried out by using Rietica software. Magnetic susceptibility measurements were carried out using a Quantum Design MPMS5 magnetometer in the temperature range 5–300 K. Approximately 20–40 mg of material was weighed accurately into a gelatin. Measurements were made on warming in a field of 1 kOe, first after cooling in zero field (ZFC) and then again after cooling in the measuring field (FC). The electrical resistivity and thermoelectric property were measured using a Quantum Design physical properties measurement system (PPMS). The electric structure was obtained from first-principles density functional theory (DFT) in the generalized gradient approximation (GGA) according to Perdew et al. [23], which were calculated using the plane-wave projector augmented method as implement in the Vienna ab initio simulation package (VASP). An energy cut-off of 520 eV was used. The convergence criterion energy was set to be 10^{-6} eV per unit cell and the forces on all relaxed atoms were less than 0.01 eV Å^{-1}.

3. Results and discussion

The structure of Bi2LnO4Cu2Se2 is shown in figure 1, which can be described as stacking of edge-shared Cu2Se2 tetrahedron layers with Bi2LnO4 layers alternatively along the c-axis. The Bi2LnO4 layer can be described as ‘[M2O4]+’ layer, which is a double fluorite-type slab. The [M2O4]+ units have been observed in several series of copper oxide superconductors, for example (Ce,Ln)Sr2Cu3O11 and (Y, Ce)3SrCuFeO9 [24–26]. On the other hand, this type of oxyselenides has a similar structure to the oxyhalides. The structure of BiOCuSe is derived from that of PbFCl or BiOCl through the replacement of chloride by selenide and the incorporation of the Cu+ ions into tetrahedral sites coordinated by selenide ions. Thus, the ZrSiCuAs structure of La(Bi)OCuS(Se) is also often described as the stuffed or
filled PbFCl structure. The relation between Bi$_2$NdO$_4$Cl and Bi$_2$NdO$_4$Cu$_2$Se$_2$ is different from that of BiOCl and BiOCuSe (electronic supplementary material, figure S1). In fact, the unit cell of Bi$_2$NdO$_4$Cu$_2$Se$_2$ can be regarded as double units of BiOCuSe, which are connected by the vertical Bi-site atoms but placed in opposite directions along c-axis. Figure 1b shows the Bi$_2$LnO$_4$ layers from a vertical view. The Ln ions located in square-planar environments in this compound, which provide a model of two-dimensional physical properties of the rear earth element. Figure 1c shows the Cu$_2$Se$_2$ tetrahedral structure.

We successfully synthesized a series of Bi$_2$LnO$_4$Cu$_2$Se$_2$ (Ln = Nd, Sm, Eu, Dy, Er, Yb), in which the Nd, Sm analogues were first synthesized by Evans et al. [21] and the Eu, Dy, Er, Yb analogues are reported for the first time. All the samples are black, which is consistent with their electric transport properties in the following. Figure 2 shows the powder X-ray diffraction (XRD) patterns of Bi$_2$LnO$_4$Cu$_2$Se$_2$, scanning over a 2θ range of 10–90° at room temperature. Using the tetragonal structure with the space group of I4/mmm, the XRD patterns for the whole compounds can be fitted very well, which are shown with red lines in figure 2. (The details are shown in the electronic supplementary material.) With the Ln ion changing from Nd to Yb, the diffraction peaks gradually shift to higher angle degree, suggesting a contraction of the lattice. The results obtained from the refinement of the X-ray diffraction data are shown.
in tables 1–3. It can be seen that when the Ln changes from Nd to Yb, the lattice parameters a and c decrease correspondingly, which can be explained by the decrease of the ionic sizes of Ln. Bond lengths provide information about the nature of the chemical bonds. The measured bond length \( d \) of an ideal ionic bond is close to the estimated bond length given by the sum of the ionic radii of a cation (\( d_c \)) and a neighbouring anion (\( d_a \)). The length of the Cu-Se bond was nearly equal in \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \) ranging from 2.42 to 2.45 Å. But the length of Cu-Se bond is shorter than that in \( \text{BiOCuSe} \) (2.51 Å) and \( \text{LaOCuSe} \) (2.52 Å) [27]. The Cu ion in the semiconducting \( \text{BiOCuSe} \) and \( \text{LaOCuSe} \) is monovalent. The Cu in \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \) should be in a higher valence state than in \( \text{BiOCuSe} \), because the ionic radii of \( \text{Cu}^{2+} \) is shorter than that of \( \text{Cu}^+ \). The bond length indicates that the Cu cation provides more electrons to the neighbouring Se anion. Our previous results have indicated the existence of a mixed-valence state of \( \text{Cu}^{2+}/\text{Cu}^+ \) in \( \text{Bi}_2\text{YO}_4\text{Cu}_2\text{Se}_2 \), which causes the metallic behaviour in this compound. The Bi-O bond lengths in \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \) are shorter than that in \( \text{BiOCuSe} \) (2.33 Å) [27], which suggests the Bi-O has greater covalent character. On the contrary, the Bi-Se bond in \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \) lengths are longer than that in \( \text{BiOCuSe} \) (3.23 Å) [27], indicating the Bi-Se bond are weaker. These observations indicate the two-dimensional nature of \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \) is stronger than that in \( \text{BiOCuSe} \).

Recently, we studied the physical properties of the analogue \( \text{Bi}_2\text{YO}_4\text{Cu}_2\text{Se}_2 \). The theoretical calculation indicated that the ground state of this compound is the quasi-two-dimensional metal state. The states of the valence band maximum are mainly composed of antibonding Cu-3d/Se-4p states and the conduction band are mainly Bi-6p/O-2p states. When the transferred valence electrons from the blocking layer to Cu-Se layer are less than two per layer, the compound would exhibit metallic behaviours. The electric transport properties of \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \) are shown in figure 3. All these compounds show metallic behaviours in the measured temperature region, which agrees with the conclusion we obtained from theoretical calculations. For all the samples, the resistance drops linearly from 300 to 100 K. The influence of Ln atoms to the transport properties is mainly embodied in the influence of the structure of the Cu-Se layer. As the Ln atom changed from Nd to Yb, the size of which is decreasing, the angle of Se-Cu-Se and the distance of Cu-Cu tend to decrease. As a result, the electrons transferred easily in Cu-Se layers. This can be demonstrated by the decreasing resistivity and smaller temperature coefficient of resistivity as Ln changing from Nd to Yb. At low-temperature region, the resistance is satisfied with the Fermi-liquid behaviour in the ground state and we fitted the resistance curve using the equation \( \rho = \rho_0 + A T^2 \), where \( \rho_0 \) is the residual resistivity, and the coefficient \( A \) represents the inelastic scattering between electrons and is generally proportional to the square of the effective electron mass. (The values of the fitted \( \rho_0 \) and \( A \) are shown in electronic supplementary material, table S1.) We also measured the thermoelectric transport properties of all the samples. The Seebeck coefficients are positive in the whole measured temperature region, indicating the major carriers are holes for all the samples. (The measured Seebeck coefficient \( S \), thermal conductivity \( \kappa \), electrical conductivity \( \sigma \) and figure of merit \( ZT = S^2T/\kappa \) at room temperature are shown in electronic supplementary material, table S2.)

We measured the magnetic properties of the samples. Plots of the temperature dependence of the magnetic susceptibility for \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \) (Ln = Sm, Nd, Eu, Dy, Er, Yb) are shown in electronic supplementary material, figure S3. These samples have relatively high susceptibility compared with \( \text{Bi}_2\text{YO}_4\text{Cu}_2\text{Se}_2 \). The order of susceptibility from large to small is Dy, Er, Yb, Nd and Sm, which is related to the occupation of the 4f orbital in the Ln ions. All the measured samples exhibit paramagnetic behaviour in the measured temperature region from 5 to 300 K. For Dy and Eu analogues, the inverse susceptibility curves are relatively linear with temperatures nearly in the whole measured temperature region, which could be fitted by the normal Curie–Weiss law, \( \chi = C/(T - \theta_p) \). For Nd and Yb analogues, their susceptibility curves obey the Curie–Weiss law only in the higher temperature regions, and the inverse susceptibility curves deviate from linearity at low temperatures.

| Table 1. Fractional atomic coordinates of \( \text{Bi}_2\text{LnO}_4\text{Cu}_2\text{Se}_2 \). |
|-----------------|-----------------|-----------------|-----------------|
| **atom**        | \( x \)         | \( y \)         | \( z \)         |
| Bi              | 0.5             | 0.5             | \( z(\text{Bi}) \) |
| Ln              | 0.5             | 0.5             | 0.5             |
| O               | 0               | 0.5             | \( z(\text{O}) \) |
| Cu              | 0               | 0.5             | 0.25            |
| **space group** | **14/mmm**      |                 |                 |
Table 2. Results of powder X-ray diffraction and Rietveld refinements for Bi$_2$LnO$_4$Cu$_2$Se$_2$ at room temperature.

| formula          | Bi$_2$NdO$_4$Cu$_2$Se$_2$ | Bi$_2$SmO$_4$Cu$_2$Se$_2$ | Bi$_2$EuO$_4$Cu$_2$Se$_2$ | Bi$_2$DyO$_4$Cu$_2$Se$_2$ | Bi$_2$ErO$_4$Cu$_2$Se$_2$ | Bi$_2$YbO$_4$Cu$_2$Se$_2$ |
|------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| molecular weight | 911.210                   | 917.330                   | 918.934                   | 929.470                   | 934.230                   | 940.010                   |
| lattice space group | tetragonal                | tetragonal                | tetragonal                | tetragonal                | tetragonal                | tetragonal                |
| a (Å)            | 3.9175(3)                 | 3.9003(2)                 | 3.8957(2)                 | 3.8695(2)                 | 3.8570(3)                 | 3.844(2)                  |
| c (Å)            | 24.525(2)                 | 24.495(2)                 | 24.439(1)                 | 24.435(2)                 | 24.440(2)                 | 24.424(2)                 |
| V (Å$^3$)        | 376.38(5)                 | 372.62(4)                 | 370.35(3)                 | 365.87(3)                 | 363.58(4)                 | 360.89(4)                 |
| D (g cm$^{-3}$)  | 8.037                     | 8.172                     | 8.237                     | 8.433                     | 8.530                     | 8.647                     |
| Rp (%)           | 7.837                     | 7.058                     | 5.390                     | 7.534                     | 8.004                     | 7.666                     |
| Rwp (%)          | 7.632                     | 5.957                     | 4.746                     | 5.911                     | 6.518                     | 6.331                     |
| $\chi^2$        | 2.437                     | 1.592                     | 1.840                     | 1.760                     | 1.940                     | 2.421                     |

$R_p = \sum |y_o - y_c| / \sum |y_o|$, $R_{wp} = \left[ \frac{\sum w(y_o - y_c)^2}{\sum w y_o^2}\right]^{1/2}$, $\chi^2 = \sum [w(y_o - y_c)^2]/(N - P_1 - P_2)$
The magnetic behaviour of Bi₂SmO₄Cu₂Se₂ is not remarkable and the inverse susceptibility curve for Bi₂SmO₄Cu₂Se₂ is convex, indicating the itinerant electron susceptibility is non-negligible. We fitted the susceptibility curve in the whole measured temperature range using the modified Curie–Weiss law, \( \chi = C/(T - \theta_p) + \chi_0 \). We calculated the effective moment from the fitted parameters which are plotted in electronic supplementary material, figure S3. These values are all consistent with the expected values for the trivalent Ln free ions, which can be expressed as \( m = g \sqrt{J(J+1)} \). All the Weiss constants are negative, suggesting antiferromagnetic exchange interactions, but further measurements are required for more detailed interpretation.

In order to verify the metallic ground state, we studied the density of states (DOS) and the band structure of Bi₂NdO₄Cu₂Se₂ calculated using DFT. The crystal structures of Bi₂LnO₄Cu₂Se₂ were optimized with respect to the lattice parameters and atomic positions. All the optimized lattice parameters and atomic coordinates are in good agreement with the experimental observation. The calculated DOS of Bi₂NdO₄Cu₂Se₂ is shown in figure 4a. There is finite DOS at the Fermi level, indicating the metallic ground state. The valence band maximum of Bi₂NdO₄Cu₂Se₂ mainly consists of Cu-3d and Se-4p electrons. The conduction band minimum is mainly built up of Bi-6p and O-2p electrons. Figure 4b shows the band structure of Bi₂NdO₄Cu₂Se₂. There are two bands crossing the \( E_F \) and the \( E_F \) locates at the valence band, indicating the metallic ground state and the hole-type carriers. There is a small gap between the valence band and conduction band at \( \Gamma \) point. Other Bi₂LnO₄Cu₂Se₂ have similar band structures which are not shown here.
4. Conclusion

In summary, we have synthesized a new series of layered oxyselenides Bi$_2$LnO$_4$Cu$_2$Se$_2$ through solid-state reaction. Their crystalline structures were studied through X-ray diffraction experiment. These compounds were crystalline in tetragonal structure with space group I4/mmm. All these compounds exhibit metallic transport property with hole-type carriers, which is verified by the DFT calculation. All the samples exhibit paramagnetic behaviour and no magnetic transition was found from 5 to 300 K. The new Bi$_2$LnO$_4$-type block in these compounds may give people some enlightenment in synthesizing new iron-based superconductors or other layered compounds.

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material.

Authors’ contributions. S.T., C.G. and C.W. carried out the solid-state reaction experiment, participated in data analysis, participated in the design of the study and drafted the manuscript; Q.J., G.Y. and M.S. carried out the crystal structure and physical properties analyses and critically revised the manuscript; F.X. and R.C. collected field data and critically revised the manuscript; S.T. and Y.S. conceived of the study, designed the study, coordinated the study and helped draft the manuscript. All authors gave final approval for publication and agree to be held accountable for the work performed therein.

Competing interests. There are no conflicts to declare.

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