Metal–semiconductor transition in novel layered oxychalcogenides

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Abstract

Magnetic and electrical properties were characterized for newly synthesized La$_{1-x}$Sr$_x$OCuSe ($0 < x < 0.25$) and La$_{1-x}$Ba$_x$OCuTe ($0 < x < 0.3$). Magnetic measurement showed paramagnetic behavior, but it did not obey the Curie–Weiss law, and an ordered phase was not observed down to 1.8 K in the Se and Te systems. The electrical properties of La$_{1-x}$Sr$_x$OCuSe indicated a metal–semiconductor transition at approximately $x = 0.05$ and a metallic state of a higher concentration range $x$. The electrical conductivity of La$_{0.8}$Sr$_{0.2}$OCuSe was 209 S cm$^{-1}$ at room temperature. In La$_{1-x}$Ba$_x$OCuTe, electrical resistivity systematically decreased with increasing $x$ and semiconductive behavior was observed for all $x$ values. Metal–semiconductor transition is probably caused by the degree of orientation and difference of acceptor levels in this system.

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1. Introduction

After the discovery of high-$T_c$ superconductivity in copper-based materials, it has been widely accepted that superconductivity can be realized in the two-dimensional CuO$_2$ network with a strong correlation. It is important, therefore, to investigate the physical properties of other layered compounds containing copper layers. As one such candidate, LaOCuCh (Ch = S, Se, Te) has a two-dimensional CuO$_2$ network, which is similar to that of high-$T_c$ superconducting oxides.

LaOCuCh (Ch = S, Se, Te) has a tetragonal structure (space group: P4/nmm), which is of the LaOAgS type [1] (Fig. 1). LaO and CuCh layers are stacked alternately along the c-axis and can be visualized as PbO-type and anti-PbO-type layers, respectively. The LaOAgS-type structure can be changed using a variety of rare earth metals [2], transition metals [3] and pnictogen instead of chalcogen [4,5]. In particular, the physical properties of La$_{1-x}$Ca$_x$OCu$_{1-x}$NiS and La$_{1-x}$Sr$_x$OCuS were investigated [6]. In La$_{1-x}$Ca$_x$OCu$_{1-x}$NiS, a semiconductor-to-metal transition was observed at $x = 0.03$ [7] and the origin of this metal–semiconductor transition was studied by XPS [8] and NMR [9]. In Cu 2p XPS spectra, very weak peaks corresponding to the satellite peaks of Cu$^{2+}$ are observed in La$_{1-x}$Ca$_x$OCu$_{1-x}$NiS in addition to the main peaks.

The intensity of these satellite peaks increases with $x$ for La$_{1-x}$Ca$_x$OCu$_{1-x}$NiS. In the NMR study, $^{65}$Cu-$T_1$ follows the Korringa relation, suggesting that the system is in the metallic state. The DOS at the Fermi level increases with $x$, which suggests that the metal–semiconductor transition is characterized by the filling of holes in the Cu-3d band of the oxy sulfide La$_{1-x}$Ca$_x$OCu$_{1-x}$NiS. Recently, LaOCuS has been found to be a transparent semiconductor, which shows p-type conductance controllable by acceptor doping and is expected to be used in optoelectronic applications [10,11]. However, except for these compounds, there are a few reports on the physical properties of these materials. From this point of view, we concentrated on the electrical resistivity and magnetic properties of LaOCuCh (Ch = S, Se, Te). In this paper, we report on the physical properties of La$_{1-x}$Sr$_x$OCuSe and La$_{1-x}$Ba$_x$OCuTe, in particular focusing on the metal–semiconductor transition of this system.

2. Experimental details

The samples were prepared by the solid state reaction of the starting materials, La (99.9%), La$_2$O$_3$ (99.9%), SrO (99.9%), BaO$_2$ (99.9%), CuO (99.9%), Cu (99.9%), Se (99.9%) and Te (99.999%). La$_2$O$_3$ powder was heated at 1000 °C to remove hydroxides.

We used La$_2$O$_3$, La, SrO, Cu and Se for La$_{1-x}$Sr$_x$OCuSe. Stoichiometric amounts of starting materials were mixed under an Ar atmosphere. The pressed powders were sealed in an
evacuated quartz tube and heated at 900 °C (1100 °C) for 40 (20) h for La1-xSrOCuSe.

For La1-xBaOCuTe, the starting materials and sintering conditions were different from those above. We used La, BaO2, CuO and Te and heated at 300 °C for 40 h. The pellets were ground, pressed once again, and heated at 700 °C for 40 h.

The polycrystalline samples were examined by powder X-ray diffraction using a conventional X-ray spectrometer with a graphite monochromator (RINT-1000 RIGAKU) and the intensity data were collected with Cu Kα radiation over the 2θ range from 5 to 60° with a 0.02° step width. The magnetic susceptibility measurement was performed with a SQUID magnetometer (MPMSR2 Quantum Design Co., Ltd). The electrical resistivity was measured by a conventional DC four-probe method in the temperature range between 2.0 and 300 K and performed with the PPMS (Quantum Design Co., Ltd).

3. Experimental results and discussion

The La1-xSrOCuSe samples heated at 900 and 1100 °C were found to have a (LaO)AgS-type structure through the X-ray diffraction measurements. A single phase sample was obtained for x < 0.25, but a small amount of La2O2Se or SrO was detected for x = 0.30. The lattice constants were unchanged with Sr substitution. This can be interpreted to suggest selenium deficiency. The (001) peak of the sample synthesized at 1100 °C is stronger than those synthesized at 900 °C. This suggests that the 1100 °C sample is oriented along the c-axis.

The magnetic susceptibility measurement for La1-xSr0.1OCuSe (900 and 1100 °C) showed paramagnetic behavior that did not obey the Curie–Weiss law and did not show systematic change with Sr substitution. This paramagnetism is partly due to the Pauli-paramagnetism based on free electrons and also diamagnetism based on the closed shell-structure.

Figs. 2 and 3 show the electrical resistivity of La1-xSrOCuSe heated at 900 and 1100 °C, respectively. As shown in Fig. 2, semiconducting behavior was observed for x < 0.05. In the high temperature range, their temperature dependence obeyed the thermal-activation type law (ρ ~ \exp(E/\k_B T)) . On the other hand, the electrical resistivity at a low temperature obeyed the two-dimensional variable-range hopping law (ρ ~ \exp((T_0/T)^{1/3})). We conclude that the system is a degenerate semiconductor, because the resistivity was well fitted by 2D VRH conduction at a low temperature. For 0.05 < x < 0.30, metallic behavior was observed and electrical resistivity decreased with increasing x. The electrical resistivity was well fitted by a $T^{1.5}$ temperature dependence, which suggests that La1-xSrOCuSe becomes a non-Fermi liquid state. As shown in Fig. 3, a metal-semiconducting transition was observed from 0.025 to 0.05 and the transition temperature decreased with increasing x. For x > 0.05, metallic behavior was observed and the electrical conductivity of La0.8Sr0.2OCuSe was 209 S cm$^{-1}$ at room temperature. This value is higher than that of Mg-doped LaOCuSe epitaxial films [12].

On the other hand, Ohtani et al. reported the metal–semiconductor transition in La0.8Sr0.2OCuSe, and which was synthesized at 500 °C, semiconducting behavior was observed for x = 0.05–0.10 [13]. This electrical resistivity difference under the different sintering conditions can be interpreted on the basis of the two-dimensional anisotropic structure and the degree of orientation. LaOCuCh has, because of a layered structure, a strong anisotropic conductivity. If the samples have different c-axis orientations under different sintering conditions, it will be easy understood to show their different electrical resistivities. We synthesized the samples under the conditions of 500, 900, and 1100 °C to examine their different c-axis orientations. For the sample synthesized at 500 °C, the (004) peak was not observed. On the other hand, the (004) peak was observed for the samples synthesized at 900 and 1100 °C.
In addition, the (004) peak of the sample synthesized at 1100 °C had a stronger intensity than that at 900 °C. We found that the c-axis orientation increased with sintering temperature. So, we conclude that the different resistivities of the three samples are due to the anisotropic conductivity and degree of orientation.

The La$_{1-x}$Ba$_x$OCuTe was found to have a (LaO)AgS-type structure by X-ray diffraction measurements. Single-phased samples were obtained for all $x$. The Ba concentration dependence of the lattice constants $a$ and $c$ systematically increased with $x$ up to $x = 0.20$ and decreased with $x$ up to $x = 0.30$.

The magnetic susceptibility of La$_{1-x}$Ba$_x$OCuTe showed paramagnetic behavior such as La$_{1-x}$Sr$_x$OCuS and did not show systematic changes with Ba substitution.

The electrical resistivity of La$_{1-x}$Ba$_x$OCuTe is shown in Fig. 4 for the present system. Since it was impossible to prepare a tightly sintered ceramic specimen available for the resistivity measurement, we measured a specimen obtained by room-temperature compression. Semiconducting behavior was observed for all $x$ and showed a systematic electrical resistivity by Ba substitution. This semiconducting behavior resembles to the Se system.

Finally, we discuss the metal–semiconductor transition of oxychalcogenide system. One of the reasons of the observed difference in electrical properties between Se and Te system is the degree of orientation. The (004) peak of the Te system is very weak because we synthesized the samples under the conditions of temperature compression. Semiconducting behavior such as La$_{1-x}$Ni$_x$S, a semiconductor-to-metal transition was observed at $x = 0.03$. However, temperature dependence of resistivity is semiconductive in La$_{1-x}$Ca$_x$OCuS without Ni substitution. It suggests that acceptor levels are important to show the semiconductor-to-metal transition. To understand the metal–semiconductor transition, we propose here the model that Sr acceptor level is shallower than the Ba acceptor level. In La$_{1-x}$Sr$_x$OCuSe, an acceptor band is formed above the valence band because of the shallow acceptor level. By Sr substitutions, holes are introduced into the Cu-3d valence band and a metal–semiconductor transition is realized.

On the other hand, Ba acceptor level is deeper than the Sr acceptor level. With only Ba substitutions, holes are not introduced into the Cu-3d valence band. Usually, it is expected that Te system is easier to become metal state than Se system because of the expansion of Te orbital. However, La$_{1-x}$Ba$_x$OCuTe is semiconducting for all samples. This suggests that Ba acceptor level is deeper than the Sr acceptor level. Differences between the two acceptor levels can explain the difference in electrical properties between the Se and Te system.

### 4. Summary

We newly synthesized La$_{1-x}$Sr$_x$OCuSe ($0 < x < 0.25$) and La$_{1-x}$Ba$_x$OCuTe ($0 < x < 0.3$). The magnetic susceptibility was paramagnetic, however, it did not obey the Curie law in each system. In La$_{1-x}$Sr$_x$OCuSe, we observed the metal–semiconductor transition for $x < 0.05$. The electrical conductivity is $209 \, \Omega \cdot \text{cm}$ for $x = 0.2$ at room temperature, indicating that this material is a good candidate for optical applications. In La$_{1-x}$Ba$_x$OCuTe, semiconducting behavior was observed and electrical resistivity systematically decreased with $x$. The origin of the metal–semiconductor transition was discussed based on the degree of orientation and the difference in acceptor level.

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