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XPS study of layered oxysulfides $(La_{1-x}Ca_xO)Cu_{1-y}Ni_yS$ ($y=0$ and $y=x$)

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Abstract

LaOCuS is a semiconductor with a layered structure in which the LaOLa and SCuS layers are stacked on one other. In $(La_{1-x}Ca_xO)CuS$, in which La is substituted by Ca, the electrical resistivity decreases drastically with x, but metallic electrical conductivity is not observed. In $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$, in which Cu and La are simultaneously substituted by Ni and Ca, respectively, the conductivity increases remarkably with x, and a metal–insulator transition occurs at $x=0.03$. In the Cu 2p XPS spectra, very weak peaks corresponding to the satellite peaks of Cu^{2+} are observed in LaOCuS in addition to the main peaks. The intensity of these satellite peaks increases with x for $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$, while it hardly changes with x for $(La_{1-x}Ca_xO)CuS$. In the S 2p XPS spectra, marked changes have not been observed for either system. This indicates that Cu^{2+} is formed by Ni substitution. The d holes thus introduced becomes mobile and the metal–semiconductor transition occurs at an appropriate hole concentration. For $(La_{1-x}Ca_xO)CuS$, the main site where the change of the electronic state is introduced by the substitution has not been clarified.

Keywords: Layered compounds; Oxysulfide; XPS

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1. Introduction

The characteristic feature of high-T_c superconducting oxides (HTSCO) is that the electronic state of the CuO_2 plane which bears the superconductivity is two-dimensional with a strong correlation. It is important to investigate the electrical properties of other layered compounds containing Cu layers and compare them with those of HTSCO.

Layered oxysulfide LaOCuS has the tetragonal (La-O)AgS-type crystal structure in which the LaOLa and SCuS layers are stacked on one another along the *c*-axis (Fig. 1) [1,2]. Cu ions are tetrahedrally surrounded by S ions. In this compound, Cu is monovalent ($3d^{10}$) and the Cu d band is filled and it is a semiconductor. The carrier is expected to be introduced into the SCuS layer by substituting a divalent alkaline earth ion for a La ion. We previously investigated the electrical properties of $(La_{1-x}Ca_xO)Cu_{1-y}Ni_yS$ ($y=0$ and $y=x$) [3,4]. The electrical resistivity decreased drastically with x for $(La_{1-x}Ca_xO)CuS$, but metallic electrical conduction was not observed. For $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$, in which Cu and La are simultaneously substituted by Ni and Ca, respectively, the conductivity increased remarkably with x, and the temperature dependence changes to metallic from semiconductive. A metal–insulator transition occurs at $x=0.03$. An anomalous temperature dependence, which has a local maximum, was observed in the intermediate con-

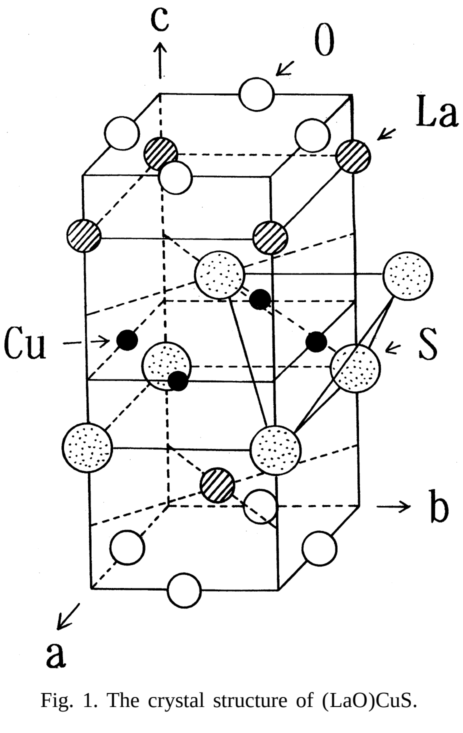

Fig. 1. The crystal structure of (LaO)CuS.

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centration range, $x=0.02$ and 0.03 [4]. In this simultaneous substitution, as La^{3+} and Cu^{+} are replaced by Ca^{2+} and Ni^{2+}, respectively, the formal valence of Cu does not change. On the other hand, as the electronic state of Ni^{2+} is $3d^8$, Ni substitution is expected to introduce holes into the d band. The process of the occurrence of metallic conduction, however, has not been made clear.

In this study, we carried out XPS measurements in order to investigate where holes are introduced. We compare these results with recent NMR results published elsewhere [5].

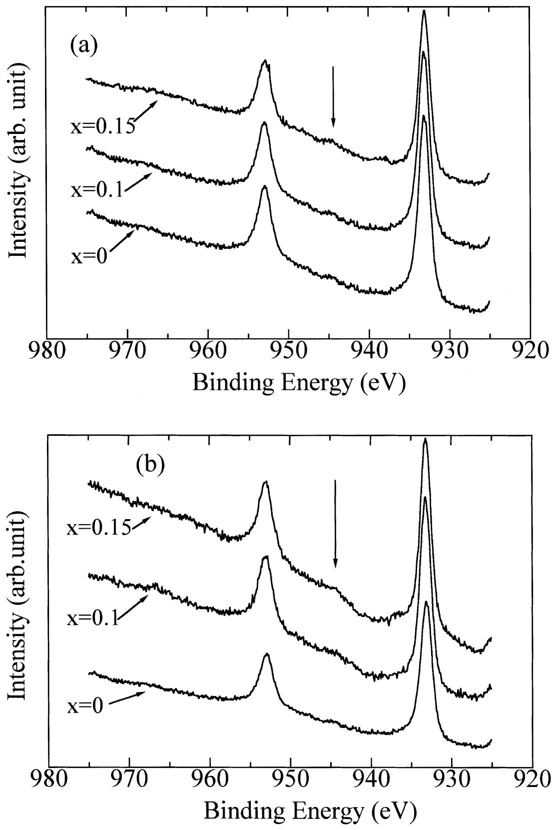

Fig. 2. The Cu 2p XPS spectra of (a) $(La_{1-x}Ca_xO)CuS$ and (b) $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$.

2. Experimental

All samples were prepared by solid state reaction. Stoichiometric amounts of La_2O_3, La_2S_3, CaO, Cu_2S, S and NiS powders were thoroughly mixed in an Ar atmosphere. Powders of La_2O_3 and CaO were preheated at 1173 K for 10 h before weighing to remove hydroxides and carbonates. Bars of the pressed powders were sealed in an evacuated quartz tube (~10^{-3} Pa) and sintered at 1373 K for 20 h for $(La_{1-x}Ca_xO)CuS$ and at 1173 K for 40 h for $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$.

XPS measurements were carried out in a vacuum of $<10^{-7}$ Pa with Mg Kα radiation (JOEL JPS-90MX). The XPS spectra were calibrated by the Ag $3d_{5/2}$ peak at 367.80 eV.

3. Results and discussion

For both the $(La_{1-x}Ca_xO)CuS$ and $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ systems, a single phase sample was obtained for $x<0.15$. Their crystal structure was confirmed to be of the (LaO)AgS-type. The lattice parameters a and c are 0.3995 and 0.8516 nm, respectively, and are almost unchanged with x.

The Cu $2p_{3/2}$ and $2p_{1/2}$ XPS spectra are shown in Fig. 2. Very weak peaks corresponding to satellite peaks of Cu^{2+} are observed even in LaOCuS in addition to the main peaks. The satellite peak of Cu $2p_{3/2}$ is indicated by the arrow. These Cu^{2+} ions are considered to be due to the off-stoichiometry of the samples which is introduced during sample preparation. The intensity of these satellite peaks increases with x for $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$, while it scarcely changes with x for $(La_{1-x}Ca_xO)CuS$. The x dependence of the intensity ratio between satellite peaks and main peaks ($I_{satellite}/I_{main}$) is shown Fig. 3. $I_{satellite}/I_{main}$ increases almost linearly with x for $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$. This result shows that Cu^{2+} are produced by the substitution. The d electron deficient state of Ni^{2+} ($3d^8$) extends to Cu ions and holes are introduced in the d band. According to the conductivity data, the metal–insulator transition occurs at $x=0.03$ for $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$. The corresponding value of $I_{satellite}/I_{main}$ is about 0.037. When $I_{satellite}/I_{main}$ exceeds this critical value, holes become mobile and the metal–insulator transition occurs. In $(La_{1-x}Ca_xO)CuS$, Cu^{2+} are not produced even with maximum substitution.

The S $2p_{3/2}$ and $2p_{1/2}$ XPS spectra are shown in Fig. 4. The binding energy is about 162 eV, which is a typical value for metal sulfides. The lines are broadened and the splitting of the $2p_{3/2}$ and $2p_{1/2}$ peaks is not observed clearly. For some samples, a small peak is observed at

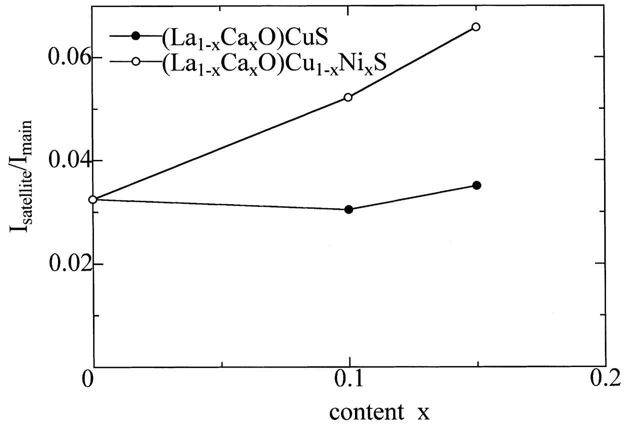

Fig. 3. The x dependence of the peak intensity ratio ($I_{satellite}/I_{main}$) for $(La_{1-x}Ca_xO)CuS$ and $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ systems.

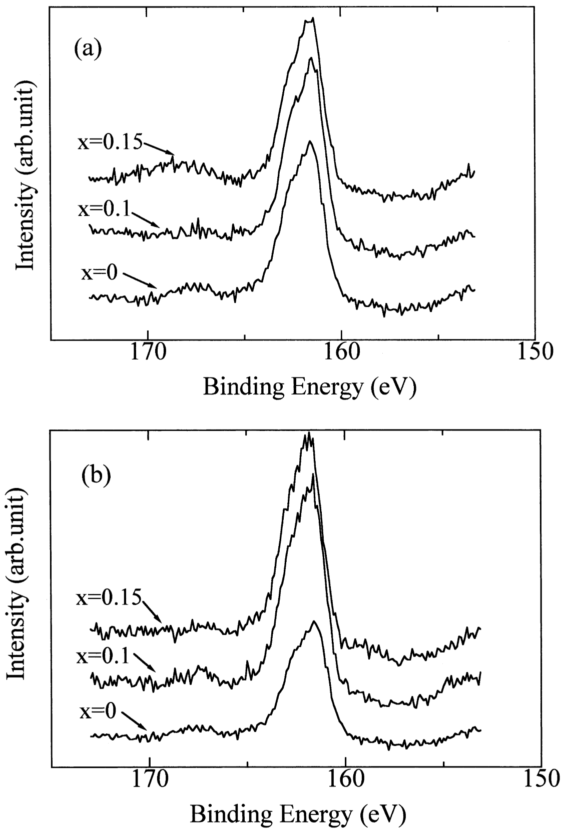

Fig. 4. The S 3p XPS spectra of (a) $(La_{1-x}Ca_xO)CuS$ and (b) $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$.

about 168 eV, which is usually observed for sulfates or highly oxidized S ions. This peak is considered to be due to S ions at the surface of the samples. In the S 2p XPS spectra, systematic changes were not observed for both systems.

According to an NMR measurement of ^{63}Cu in $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ [5], the relaxation process of ^{63}Cu is confirmed to be a quadrupole process at $x=0$, while the magnetic process dominates at $x=0.1$ at low temperature. The ^{63}Cu spin-lattice relaxation time T_1 at $x=0.1$ at low temperature roughly follows the Korringa relation of $T_1T=$ ~50 (sK), suggesting that the system is in a metallic state. However, this value is much larger than that observed for Cu metal. As the value of $(T_1T)^{-1/2}$ relates directly to the density of states (DOS) at the Fermi level, the DOS at Cu sites in the metallic state is considered to be very poor. The NMR measurement of ^{139}La suggests nearly-zero DOS at La sites in the metallic samples. The results of NMR measurement suggest that holes are introduced in S atoms. This is not confirmed by the present XPS measurements.

It is rather difficult to introduce holes into the Cu plane of LaOCuS, which is a filled band insulator, by substituting the divalent ion for a rare earth ion, compared with HTSCO. It was possible to introduce holes into the valence band by substituting Ni directly for Cu. The hole concentration is lower than the amount of Ni substitution. On the other hand, in HTSCO, which is a Mott insulator, when the divalent ion is substituted for a rare earth ion, holes are introduced rather easily in the CuO_2 plane and the metal–insulator transition occurs.

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