Journal of Alloys and Compounds 408–412 (2006) 95–97

Journal of ALLOYS AND COMPOUNDS

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# Structural studies of Ca and transition metal co-doped system $(La_{1-x}Ca_xO)Cu_{1-x}M_xS$ (M = Mn, Co, Ni, Zn)

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## Abstract

We have precisely investigated the crystal structure of various doped samples of $(La_{1-x}Ca_xO)Cu_{1-x}M_xS$ (M = Mn, Co, Ni, Zn) in order to understand changes of the electrical properties from a view point of the crystal structure. The distance between LaO and CuS layers along *c*-axis, $d_{La–S}$ increases with increasing electrical resistivity of $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ and it approaches a value of insulating samples, $(La_{1-x}Ca_xO)Cu_{1-x}M_xS$ (M = Mn, Co, Zn). The changes of the electrical properties is considered to be due to the charge transfer between LaO and CuS layer which is caused by the change of $d_{La–S}$.

*PACS:* 72.20.-i; 61.10.Nz

*Keywords:* Oxysulfide; (LaO)CuS; Layer structure; Structure studies; Electrical resistivity

## 1. Introduction

Wide gap semiconductors are useful materials in applications as transparent conductive, light emitting and photovoltaic materials. Furthermore, theoretical studies predicted room temperature ferromagnetism of wide gap p-type semiconductors [1,2]. The layered oxysulfide (LaO)CuS is one of the transparent p-type semiconductors. Fig. 1(a) shows the crystal structure of (LaO)CuS in which two types of layers, CuS and LaO, alternate along the *c*-axis. Its crystal structure is tetragonal and belongs to the space group $P4/nmm$ [3]. The CuS layer in which Cu ion is surrounded tetrahedrally by four S ions is expected to form a two dimensional conductive layer and the LaO layer in which O ion is also surrounded tetrahedrally by four La ions is expected to form a two dimesional insulative layer. Fig. 1(b) shows the view from *a*-axis. In the previous works, it was found that the electrical resistivity $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ changes from semiconductive property to metallic one with increasing $x$ [4,5]. The changes of the electrical properties are understood in terms of the appearance of new density of states from the Ni 3*d* band [6]. A ferromagnetic state with the Curie temperature exceeding room temperature also is observed [7]. In this work, we have investigated the crystal structures of $(La_{1-x}Ca_xO)Cu_{1-x}M_xS$ (M = Mn, Co, Ni, Zn) and analyzed in detail to reveal the mechanism of the electrical properties by synchrotron X-ray diffraction.

## 2. Experimental

All samples were polycrystals synthesized by a solid state reaction of starting materials listed in Table 1. The common powder materials, $La_2S_3$, $La_2O_3$, are excluded from the list. [Ca, M] (M = Mn, Co, Ni, Zn) in Table 1 means abbreviation for $(La_{1-x}Ca_xO)Cu_{1-x}M_xS$ (M = Mn, Co, Ni, Zn). Powder materials $La_2O_3$ and CaO were preheated at 950 °C

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doi:10.1016/j.jallcom.2005.04.034

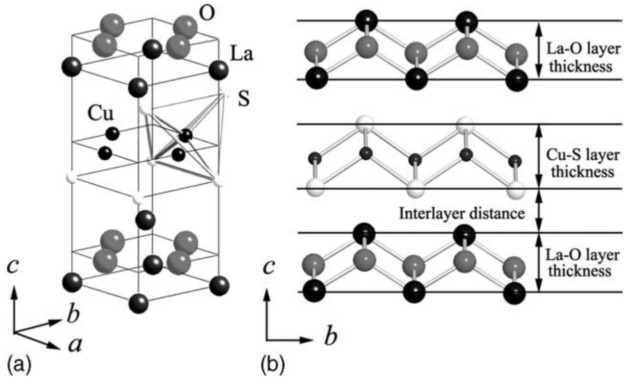

Fig. 1. Crystal structure of (LaO)CuS; (a) the unit cell, and (b) the view from *a*-axis.

Table 1
Starting materials of products of these samples

| Samples | Starting materials |
|---|---|
| (LaO)CuS | $Cu_2S$ |
| [Ca, Mn] | CaO, $Cu_2S$, MnS |
| [Ca, Co] | CaO, $Cu_2S$, CoS |
| [Ca, Ni] | CaO, $Cu_2S$, NiS |
| [Ca, Zn] | CaO, $Cu_2S$, ZnS |

for 10 h to remove hydroxides. Then, these starting materials were mixed under Ar atmosphere and pressed into rectangular bars. They were sealed in a evacuated quartz ampoules and sintered at 900 °C for 40 h. The structure and lattice parameters of the samples were characterized by the synchrotoron X-ray powder diffradtion on BL02B2 at the SPring-8. The wave length was 0.04968 nm. The exeperiments were carried out on the large Debye–Scherrer camera with transmission geometry. Diffraction patterns of the samples were recorded on the imageing plate of the camera [8]. It is possible to collect the high resolution data necessary for the more detailed analysis. Therefore we can decide on the precise fractional atomic coordinate of light element S and also find a tiny amount of impurities which exit in samples. Experimental data were analyzed by Rietveld method with RIETAN2000 program [9] in the 2$\theta$ range between 5 and 30°. The electrical resistivity measurements were performed on sintered bulk by the standard DC four-probe method for low resistivity samples and DC two-probe method for high resistivity ones.

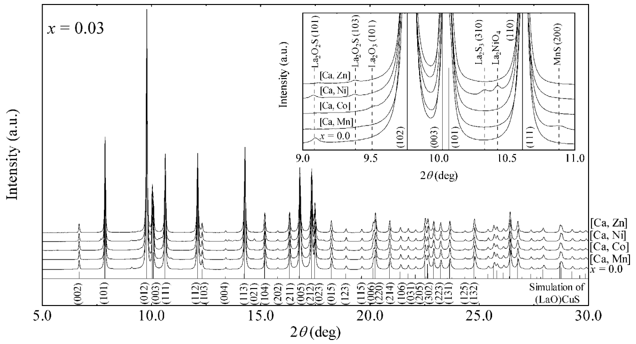

Fig. 2. X-ray diffraction patterns of various doped samples in 2$\theta$ range between 5 and 30°. The inset shows ones in 2$\theta$ range between 9 and 11°.

## 3. Results and Discussion

Fig. 2 shows the X-ray diffraction patterns for five samples, the host crystal and [Ca, M] with $x = 0.03$ togther with the calculated line position for (LaO)CuS in 2$\theta$ range between 5 and 30°. Before to the precise structural analysis, a tiny amount of impurities were checked out. The impurities were $La_2O_3$, $La_2S_3$, $La_2O_2S$, $La_2NiO_4$, ZnO and MnS. The strongest peaks of the impurity phases are much smaller (1% or less) than that of the main peak of the each samples.

Table 2 shows the lattice parameters of various samples refined by the Rietveld analysis. The lattice constants *a* and *c* of (LaO)CuS are two figures more accurate than the value reported untill now [3]. Here, La-z and S-z mean *z*-coordinates of La and S, respectively and $d_{\text{La–S}}$ is the interlayer distance between LaO and CuS layers along *c*-axis estimated from the *z*-coordinates of ones.

Fig. 3 shows the temperature dependence of the electrical resistivity of all samples. The electrical resistivity of the samples of [Ca, Ni] with $x < 0.03$ show semiconducting behavior and the others ($x \geq 0.03$) show metallic ones. The absolute values of electrical resistivity decrease with increasing *x* due to the carrier doping by cation substitution. On the other hand, the values of the electrical resistivity [Ca, Mn], [Ca, Co] and [Ca, Zn] are high and almost same in the magnitude [10]. Fig. 4 shows the relationship between the distance $d_{\text{La–S}}$ and the electrical resistivity at room temperature. The distance $d_{\text{La–S}}$ increases with increasing the electrical resistivity of [Ca, Ni] and it approaches the values of insulating samples,

Table 2
Lattice parameters characterized by the synchrotron X-ray powder diffraction

| Samples | *x* | *a* (nm) | *c* (nm) | La-z | S-z | $d_{\text{La–S}}$ (nm) | $R_{\text{wp}}$ (%) |
|---|---|---|---|---|---|---|---|
| (LaO)CuS | 0 | 0.399484(2) | 0.851254(5) | 0.14755(3) | 0.6626(1) | 0.1614(1) | 5.96 |
| [Ca, Ni] | 0.02 | 0.39959(1) | 0.85123(2) | 0.1477(1) | 0.6626(3) | 0.1615(3) | 6.30 |
|  | 0.03 | 0.39946(1) | 0.85113(2) | 0.1477(1) | 0.6631(3) | 0.1610(3) | 7.30 |
|  | 0.04 | 0.39963(1) | 0.85099(2) | 0.1477(1) | 0.6633(3) | 0.1608(3) | 7.45 |
|  | 0.05 | 0.39947(1) | 0.85106(2) | 0.1476(1) | 0.6635(3) | 0.1607(3) | 7.99 |
|  | 0.07 | 0.39953(1) | 0.85106(2) | 0.1476(1) | 0.6643(3) | 0.1600(3) | 6.77 |
| [Ca, Mn] | 0.03 | 0.39986(2) | 0.85173(3) | 0.1476(1) | 0.6625(3) | 0.1618(3) | 5.62 |
| [Ca, Co] | 0.03 | 0.39991(2) | 0.85188(4) | 0.1475(1) | 0.6623(3) | 0.1620(3) | 5.28 |
| [Ca, Zn] | 0.03 | 0.39989(2) | 0.85221(3) | 0.1474(1) | 0.6627(3) | 0.1618(3) | 5.30 |

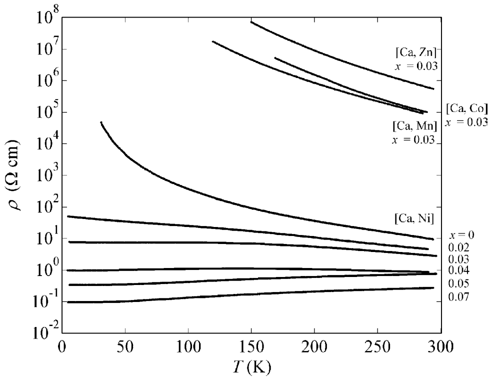

Fig. 3. Temperature dependence of the electrical resistivity of various doped samples.

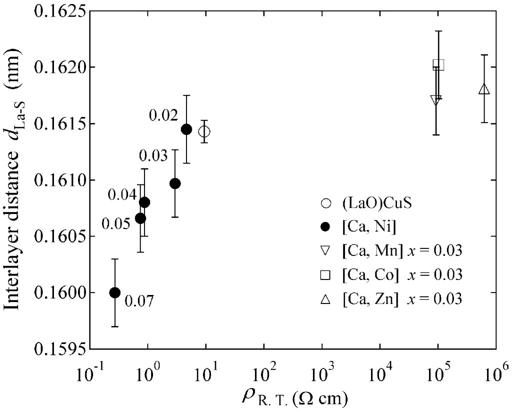

Fig. 4. The relationship between the interlayer distance $d_{La–S}$ and the electrical resistivity at room temperature.

[Ca, M] (M = Mn, Co, Zn). The change of electronic state of CuS and LaO layers by carrier doping is considered to affect the distance between both layers $d_{La–S}$. The charge transfer between LaO and CuS layers may be influenced by the change of $d_{La–S}$. The electrical properties are determined by these two factors. No charge density have been found in the interlayer space of the host material (LaO)CuS [11]. It is possible that the change of charge distribution occurs and the charge density appears in the interlayer space in the metallic samples. Therefore, the investigation of a charge density for the metallic samples is necessary to precisely understand these changes of the electrical resistivity.

## Acknowlegments

The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposals Nos. 2002B0326 and 2003B0453).

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