Charge Density Study of Transparent p-type Semiconductor (LaO)CuS

The application of transparent materials into electrically industrial materials had been limited to just electrodes for a long time because wide-gap semiconductors as transparent materials have strong monopolarity. Indeed, almost all transparent conductive oxides such as SnO_2 and In_2O_3 are n-type; thus, the lack of transparent p-type semiconductors has hindered the realization of transparent p-n junctions. Recently several p-type semiconductors such as $CuAlO_2$ and $SrCu_2O_2$ have been discovered, and considerable effort has been devoted to the fabrication of transparent devices such as a transparent light-emitting device. The further exploration of new p-type materials is still in progress.

The rare earth oxysulfide (LaO)CuS is also a transparent p-type semiconductor with a band gap of 3.1 eV. This material has various attractive functionalities, for example, it exhibits good luminescent properties in terms of photoluminescence [1,2] and room temperature ferromagnetism when La and Cu are simultaneously replaced by Ca and Ni, respectively [3]. More functionalities are expected to be added to (LaO)CuS by substitution. It is necessary to understand the chemical bonding and the ionic state of (LaO)CuS. Therefore, we have performed a charge density study with synchrotron radiation powder diffraction at beamline **BL02B2** using a large Debye-Scherrer camera equipped with an imaging plate as a highly sensitive X-ray detector [4].

Figure 1 shows the crystal structure of (LaO)CuS with the space group of P4/nmm [5]. The salient feature of this structure is that a Cu atom is surrounded tetrahedrally by four S atoms, as shown in Fig. 1(a). Figure 1(b) is the view from the a-axis which includes total eight unit cells. Zigzag layers of CuS and LaO are stacked alternately along the c-axis alternately and this semiconductor is considered having layered structure. Figure 2 shows the raw data obtained from the large Debye-Scherrer camera, the diffraction profile using a high energy X-ray with an incident wavelength of 0.4969 Å, and the fitting result obtained by Rietveld analysis. Uniform Debye-Scherrer rings are found in the data and this reveals that the data are sufficient reliable for the analysis, for the data up to 70° (d > 0.4332 Å) were used. The calculated result with reliability factors of 4.73 % in R_{wp} and 1.35 % in R_F is in good agreement with the experimental result up to higher 2θ range. The lattice constants obtained by this analysis were

3.99425 Å and 8.51046 Å for the a axis and c axis, respectively. The charge density distributions of (LaO)CuS were analyzed by the maximum entropy method (MEM)/Rietveld method to obtain information on the bonding nature. Figure 3 shows a three-dimensional view of the charge density distribution at the equi-density level of 0.4 $e/Å^3$. Contour lines are also added to the cross-sectional view, where the lines are drawn at intervals of 0.1 $e/Å^3$ from 0.4 to 0.7 $e/Å^3$ and the black color indicates the region with higher density region than 1.0 $e/Å^3$. A finite electron density is found between the Cu and S atoms and between the La and O atoms. Consequently, covalent characteristics are found in both the Cu-S bond and the La-O bond, even though the full-potential linear-augmented plane wave band calculation predicted that the Cu-S bond has a covalent character, whereas the La-O bond was ionic [6]. For the interlayer space between the CuS layer and the LaO layer, there is no marked charge density. This is the first evidence showing that this transparent semiconductor has a layered structure. The electron number is counted in the region surrounded by the minimum charge-density surfaces adopting the Mulliken scheme. The electron numbers for La, O, Cu, and S are 55.6, 9.3, 29.3, and 15.8, respectively. The ionic state is defined by subtracting the electron number from the atomic number. The results are +1.4 for ^{58}La, -1.3 for ^{2}O, -0.3 for ^{29}Cu, and +0.2 for ^{16}S. According to these values, the charges of the CuS layer and the LaO layer are electrically almost neutral. Furthermore, the Cu-S chemical bonding is perfectly covalent, whereas the La-O bonding has both ionic and covalent characteristics. These distinctive features such as the charge neutrality of each layer and the covalent
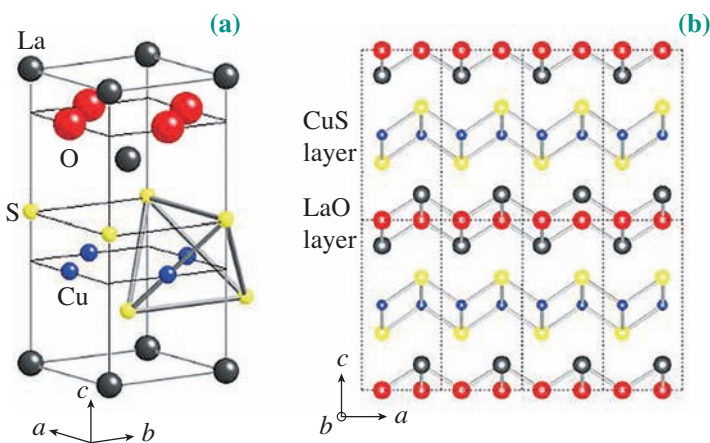

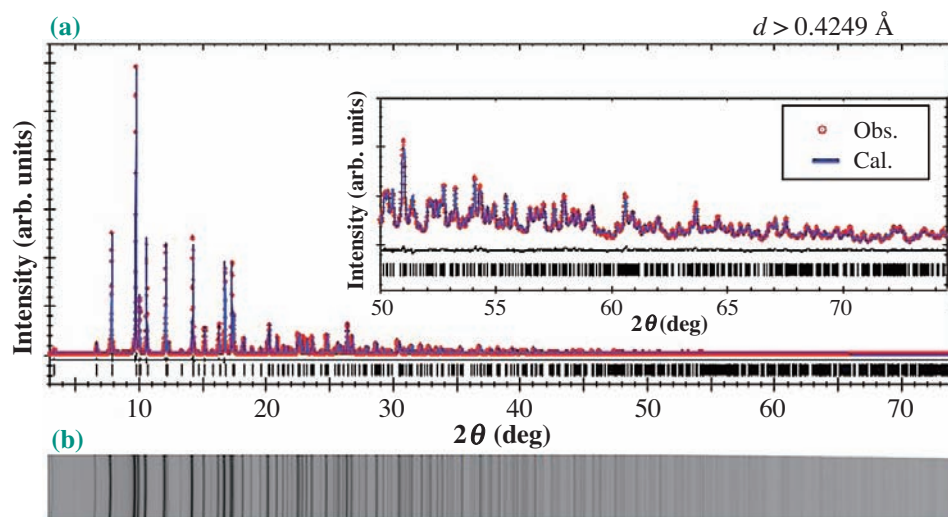Fig. 1. Crystal structure of (LaO)CuS. Unit cell **(a)** and the view from a-axis **(b)**.

(a) $d > 0.4249$ Å

Fig. 2. **(a)** Powder diffraction profile and **(b)** raw data. The dots are experimental results and the solid line is the pattern fitted by the Rietveld method with reliability factors 4.73 % in R_{wp} and 1.35 % in R_F.

character of the La-O bond may provide fascinating functionalities.

In summary, we have studied the charge density distributions of the transparent p-type semiconductor (LaO)CuS using synchrotron powder diffraction, whose data were analyzed by the MEM/Rietveld method. The Cu-S bonding was found to have a strong covalent character and the La-O bonding seems to have both covalent and ionic characteristics. The estimated ionic states of each element suggest that each layer has charge neutrality. The charge density distribution provides direct evidence of the layered structure.
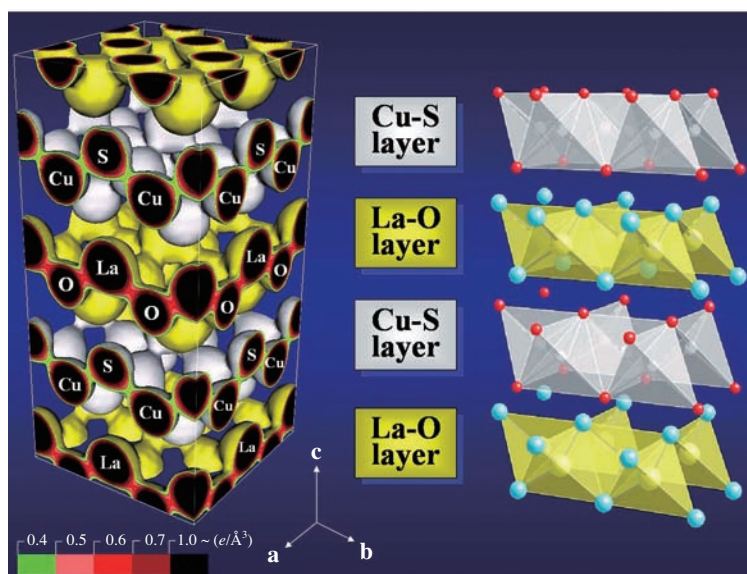

Fig. 3. Three-dimensional view of charge density distributions of (LaO)CuS at 0.4 e/Å^3 equi-density surface accompanying by contour lines, drawn from 0.4 to 0.7 e/Å^3 with an interval of 0.1 e/Å^3.

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