

## Charge density distribution of transparent *p*-type semiconductor (LaO)CuS

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The charge density distributions of layered oxysulfide (LaO)CuS, known as a *p*-type transparent semiconductor, have been investigated by analyzing the synchrotron radiation powder diffraction profile with the maximum entropy method/Rietveld method. The bonding character of the Cu–S bond is revealed to be covalent. Meanwhile, the O–La bonding has both ionic and covalent characters. The number of electrons estimated by integrating the charge density around each atom gave direct evidence that each CuS and LaO layer is electrically almost neutral. © 2007 American Institute of Physics. [DOI: 10.1063/1.2724891]

In the last decade, wide-gap semiconductors have attracted much our attention as transparent materials, luminescent materials, laser-emission materials, and magnetic semiconductors. Almost all wide-gap semiconductors are inevitably classified into *n* type, and the lack of transparent *p*-type semiconductors restricts the fabrication of *p*-*n* junctions. The discovery of *p*-type semiconductors, such as  $\text{CuMO}_2$  ( $M = \text{Al},^{1,2} \text{Ga},^3 \text{In},^{1,4}$ ) and  $\text{SrCu}_2\text{O}_2$ ,<sup>5</sup> provides material candidates for fabricating transparent devices. However, there is still a need to discover other *p*-type materials for device applications.

Layered oxysulfide (LaO)CuS is known to be a transparent *p*-type semiconductor with a band gap of 3.1 eV (Ref. 6) and no magnetic moment.<sup>7</sup> It shows excellent optical properties expected by the presence of excitons, even at room temperature.<sup>8,9</sup> This compound has a layered (LaO)AgS-type crystal structure with the space group of  $P4/nmm$ ,<sup>10,11</sup> which consists of La–O–La and S–Cu–S slabs stacked along the *c* axis alternately, as shown in Fig. 1.

Previously, we investigated the optical and electrical properties,<sup>9</sup> as well as the photoemission spectra of (LaO)CuS samples.<sup>12</sup> Electrical conductivity and photoluminescence are strongly affected by the stoichiometry of samples. An outline of the electronic structure has been obtained through photoemission spectroscopy<sup>12</sup> and the first principles band calculation.<sup>13</sup> There remains the problem, however, of the nature of the chemical bonding in this compound. Experimental investigations into its chemical bonding have not yet been performed. It is essential to know about the direct electron density distributions in the host material (LaO)CuS to understand its unique electrical and optical properties. Therefore, in this work, we conducted a charge density study with synchrotron radiation (SR) powder diffraction.

Polycrystalline samples of (LaO)CuS were prepared by solid-state reaction. Starting materials were  $\text{La}_2\text{S}_3$  (99.9%),

$\text{La}_2\text{O}_3$  (99.999%), Cu (99.99%), and S (99.99%) powders.  $\text{La}_2\text{O}_3$  was preheated at 950 °C for 10 h to remove hydroxides. These starting materials were mixed stoichiometrically under Ar atmosphere and pressed into rectangles. The rectangular bars were sealed in an evacuated silica tube and sintered at 900 °C for 40 h. The chemical composition of the sample was checked out by means of inductively coupled plasma–atomic emission spectrometry. The molar ratio for La, O, Cu, and S in (LaO)CuS was 1:1.04:1.01:0.99, respectively, where each value is normalized by that of La. We confirmed that the chemical composition of (LaO)CuS is almost the same as the nominal value within errors.

For determination of the precise crystal structure by x-ray diffraction, especially at the electron charge density levels, it is essential to collect accurate Bragg intensity data. For this purpose, high-energy SR powder diffraction experiment was conducted on the BL02B2 at SPring-8, using a large Debye-Scherrer camera equipped with an imaging plate as a highly sensitive x-ray detector. The performance of this camera is reported elsewhere.<sup>14</sup> High-energy powder diffraction frees us from the problems of extinction and absorption effects and is quite useful for samples such as (LaO)CuS,

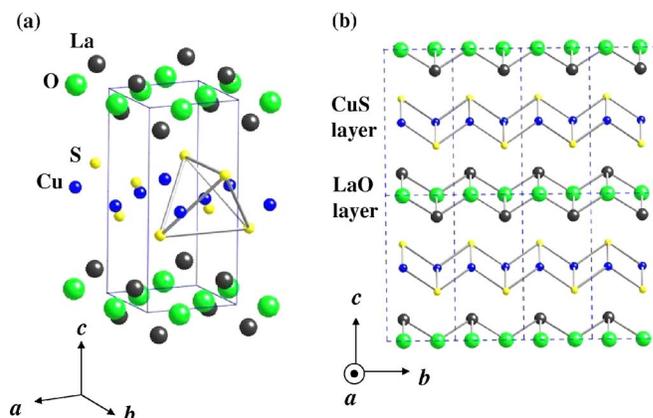


FIG. 1. Schematic diagram of the crystal structure of (LaO)CuS. The drawing in the range of unit cell (a) and the view from *a* axis (b).

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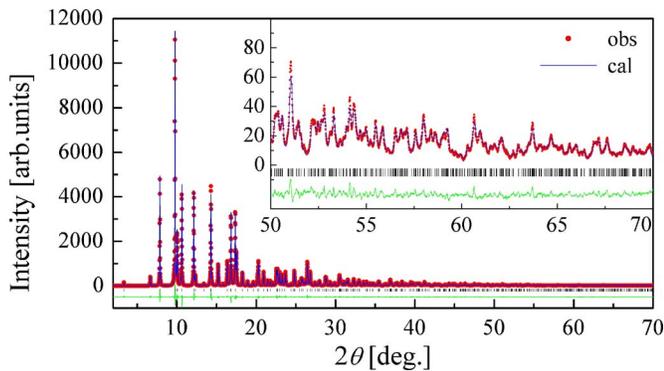


FIG. 2. SR powder diffraction pattern of (LaO)CuS. The dots denote experimental results and the solid line denotes fitted pattern by the Rietveld method. The incident wavelength of x ray is 0.4969 Å. The reliability factors are 4.73% in  $R_{wp}$  and 1.35% in  $R_F$ . The deviation between the observed intensity and the calculation is shown at the bottom of the figure with the bars which indicate peak position inherent to (LaO)CuS.

which consists of the extremely heavy element La and the light element O. The polycrystalline sample was ground into fine powders. Homogeneous granularity was achieved by the precipitation method. The powder sample was sealed in a 0.2 mm diameter silica capillary. The wavelength of the incident x rays was 0.4969 Å. To get accurate counting statistics, diffraction data were obtained at room temperature immediately before the imaging plate was saturated by the most intensive reflection. The SR powder diffraction patterns were analyzed using the maximum entropy method (MEM)/Rietveld method. The validity of the method has been demonstrated by the observation of accurate covalent bonding of silicon and diamond.<sup>15</sup> This method has also been applied to studies on the bonding character of the Pb–O bond in PbTiO<sub>3</sub>.<sup>16</sup>

Figure 2 shows a profile fitting result of the SR powder diffraction pattern obtained by the Rietveld analysis, where the space group  $P4/nmm$  was assumed and the structural parameters reported by Palazzi were used as the initial parameters.<sup>10</sup> The data used for the analysis were up to 70° ( $d > 0.4332$  Å) in  $2\theta$ . The calculated profile reproduces the experimental one well up to the higher  $2\theta$  range, as shown in the inset of Fig. 2. The reliability factors were 4.73% in  $R_{wp}$  and 1.35% in  $R_F$ . The structural parameters obtained are listed in Table I. These results are in good agreement with the data reported by Palazzi.<sup>10</sup>

The charge density distributions of (LaO)CuS were analyzed with 567 independent structure factors obtained by Rietveld analysis. The unit cell was divided into  $80 \times 80 \times 170$  pixels for  $a$ ,  $b$ , and  $c$  axes, respectively, in the MEM analysis, where the unit pixel is equal to  $0.05 \times 0.05 \times 0.05$  Å<sup>3</sup>. The program, ENIGMA,<sup>17</sup> was used for the MEM. MEM analysis accurately obtained the three dimensional (3D) charge density distribution in (LaO)CuS and provides useful information for understanding the electronic structure of this compound. The visualized charge density distributions are shown in Fig. 3 at the equidensity level of  $0.4 e/\text{Å}^3$ . The density contour line is also added in the cross-sectional view, where high-density coverage, greater than  $1.0 e/\text{Å}^3$ , is painted black and other density levels are represented by four colors. The La–O layer is yellow and the Cu–S layer is white. The covalent character is clearly observed on the bonds between O and La atoms and Cu and S atoms. The charge density distributions around Cu and S atoms are isotropic and spherically shaped in the inner core region (black color region). At the outer shell, they are anisotropic and extending along the Cu–S direction. The Cu atom is connected to four tetrahedrally surrounding S atoms by covalent bonds. Similarly, the charge density distributions around O

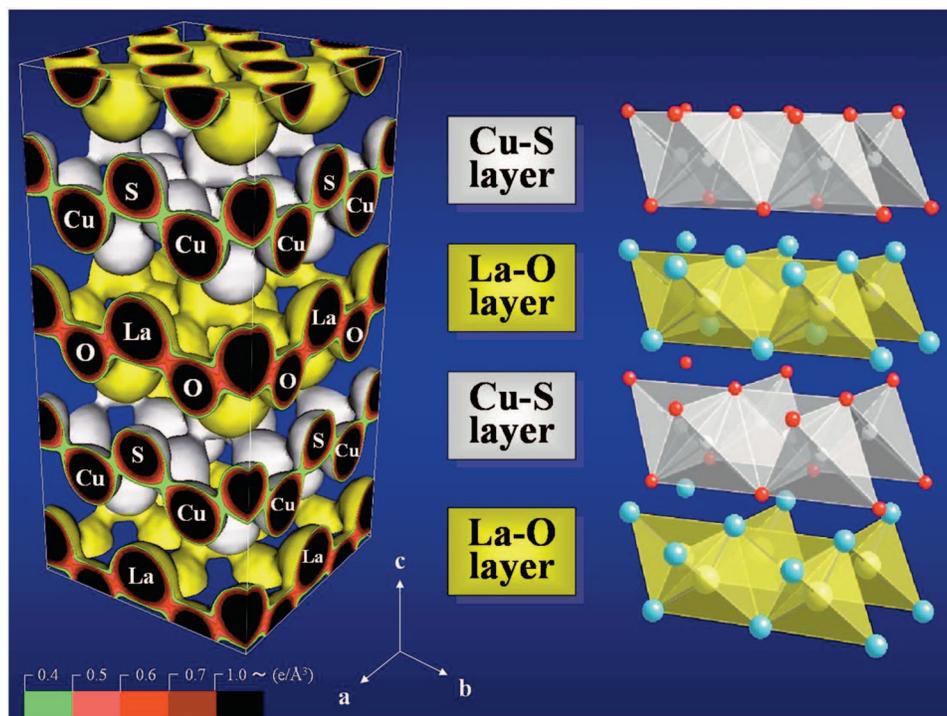


FIG. 3. (Color) Charge density distributions of (LaO)CuS derived by MEM/Rietveld analysis. The left side figure is the three dimensional (3D) view of charge density distribution. The contour lines, which are drawn from 0.4 up to  $0.7 e/\text{Å}^3$  every  $0.1 e/\text{Å}^3$  step, are superimposed on the cross-sectional view. Black color is the high-density region larger than  $1.0 e/\text{Å}^3$ . The right side figure is the schematic structure. Blue and red balls in each layer are La and S atoms, respectively.

TABLE I. Structural parameters of (LaO)CuS, where the space group  $P4/nmm$  (tetragonal system) was assumed. Off-diagonal elements of thermal parameter:  $U_{12}=U_{23}=U_{13}=0$ . Lattice constants:  $a=3.994\,25(2)$  Å and  $c=8.510\,46(7)$  Å.

Atom	$x$	$y$	$z$	$U_{11}$ (Å <sup>2</sup> )	$U_{22}$ (Å <sup>2</sup> )	$U_{33}$ (Å <sup>2</sup> )
La	0.25	0.25	0.14757(4)	0.0058(2)	0.0058(2)	0.0067(1)
O	0.25	0.75	0	0.004(2)	0.004(2)	0.006(2)
Cu	0.25	0.75	0.5	0.0210(6)	0.0210(6)	0.0229(5)
S	0.25	0.25	0.6626(1)	0.0105(7)	0.0105(7)	0.0119(8)

and La atoms are anisotropic and extend towards La and O, respectively. Our experimental results indicate that the La–O bonding also has a covalent character. The partial density of states calculated using the full-potential linearized augmented plane-wave method<sup>13</sup> predicted that the Cu 3*d* and S 3*p* states formed a well hybridized orbital, whereas the O–La bonding character was ionic. This is the direct experimental evidence indicating the covalent nature of the O–La bonding. No remarkable charge density exists in the interlayer space. The charge densities at the midpoints between S and La atoms and Cu and La atoms are almost the same as the background levels. The charge density is concentrated in the bonding network in each layer and there is no spatial extension of the charge cloud between La and S atoms.

The bonding nature, including the covalent nature of the O–La and the Cu–S bonds found in this study, gives several essential information for considering the precise electronic structure of (LaO)CuS. The electron number around each atom is counted in the region surrounded by minimum charge density surfaces adopting the Mulliken scheme. The results are 55.6, 9.3, 29.3, and 15.8 for La, O, Cu, and S, respectively. The ionic states of each atom are defined by subtracting the counted electron number from the atomic number. Each numerical value is +1.4 for <sup>58</sup>La, –1.3 for <sup>8</sup>O, –0.3 for <sup>29</sup>Cu, and +0.2 for <sup>16</sup>S. These results show that the typical ionic picture does not fit this compound. Both the O–La<sub>2</sub>–O and the S–Cu<sub>2</sub>–S layers are almost electrically neutral. A nearly zero value of the valence state for Cu and S means that the bonding between Cu and S has a strong covalent character. In contrast, the O–La bonding seems to have both ionic and covalent characters. The deviation from fully ionized states of oxygen must be attributed to the covalent nature of the La–O bond. Because each layer is almost electrically neutral, the O–La<sub>2</sub>–O and the S–Cu<sub>2</sub>–S layers are considered to be combined by the orbital widely extended over the O–La<sub>2</sub>–O and the S–Cu<sub>2</sub>–S layers and the local attraction between the La and S ions.

In conclusion, we have investigated the charge density distributions of *p*-type transparent semiconductor (LaO)CuS by analyzing the SR powder diffraction data with the MEM/Rietveld method, and found the covalent nature, not only of the Cu–S bonds but also of the O–La bonds. The estimated ionic states of each element suggest that the La–O bond has

both covalent and ionic contributions, and each layer has charge neutrality.

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