Chem. Mater. **2003,** *15,* 3692−3695

Electrical and Optical Properties and Electronic Structures of LnCuOS (Ln = La∼Nd)

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Received February 13, 2003. Revised Manuscript Received July 3, 2003

A series of layered oxysulfides, LnCuOS (Ln = La∼Nd), was studied to examine the influence of these lanthanide ions on their optical and electrical transport properties. PrCuOS and NdCuOS showed wide-gap p-type semiconducting properties similar to LaCuOS, which is a p-type semiconductor with an energy gap of 3.1 eV. A sharp photoluminescence peak near the absorption edge, which originates from excitons, was observed in LnCuOS (Ln = La, Pr, and Nd), indicating that these lanthanide ions do not influence the fundamental optical properties and excitons are confined in $(Cu_2S_2)^{2-}$ sulfide layers sandwiched between $(Ln_2O_2)^{2+}$ oxide layers. On the other hand, CeCuOS showed p-type degenerate semiconducting behavior and its color was black. The electronic structures of LnCuOS (Ln = La∼Nd) were investigated by ultraviolet photoemission spectroscopy and inverse photoemission spectroscopy to understand these differences derived from the lanthanide ions. Although no remarkable difference in the electronic structures was found among LnCuOS (Ln = La∼Nd), only an inverse photoemission spectrum of CeCuOS clearly showed an unoccupied band near the Fermi level in the conduction band. It is considered that the formation of this unoccupied band at the conduction band minimum is responsible for the unique electrical and optical features of CeCuOS.

1. Introduction

We have found wide-gap p-type conductive properties in several layered oxysulfides with $(Cu_2S_2)^{2-}$ layers.[1,2] LaCuOS, one of the layered oxysulfides, shows an energy gap as wide as 3.1 eV and exhibits p-type electrical conductivity controllable by acceptor doping from semiconducting to metallic states.[1] Moreover, a sharp luminescence peak near the absorption edge is observed under UV photoexcitation. The origin of this photoluminescence was assigned to excitons previously,[3] and the analysis of its electronic structure revealed that LaCuOS has a direct-allowed-type energy gap at Γ point.[4] To demonstrate the extension of the materials system, we recently performed band gap engineering in $LaCuOS_{1-x}Se_x$ ($0 \le x \le 1$) by the substitution of Se for S ions, maintaining the photoluminescence feature as well as the wide-gap p-type conductive properties.[5] These electrical and optical characteristics of $LaCuOS_{1-x}Se_x$ show promise as materials applicable to optoelectronic devices.

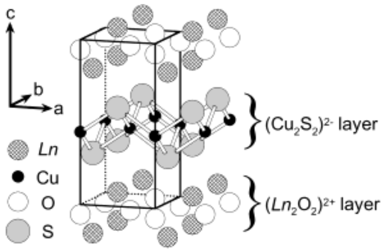

Figure 1. Crystal structure of LnCuOS (Ln = La∼Nd) composed of $(Ln_2O_2)^{2+}$ and $(Cu_2S_2)^{2-}$ layers.

LaCuOS is a mixed-anion material composed of divalent oxygen and sulfur anions. The important feature of its crystal structure is that LaCuOS crystallizes in a layered structure, and Cu^+ ions are coordinated by sulfur anions exclusively. The crystal structure of LaCuOS is shown in Figure 1. The oxide layers and sulfide layers are clearly separated in space, and the $(La_2O_2)^{2+}$ layers and $(Cu_2S_2)^{2-}$ layers are alternately stacked along the *c* axis.[6] The structure of each layer sublattice is regarded as a PbO-type for the $(La_2O_2)^{2+}$ layers and anti-PbO-type for the $(Cu_2S_2)^{2-}$ layers. This layered crystal structure brings interesting electrical and optical properties to these materials.

Several lanthanide ions (Ce, Pr, Nd, Sm, and Eu) are known to replace for La ions in LaCuOS due to the

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10.1021/cm030175i CCC: $25.00

similar size of ionic radii of these lanthanide ions.[7] In our previous paper,[8] we prepared the single phases of LnCuOS (Ln = La, Ce, Pr, and Nd) and analyzed their crystal structures. Although anomalous shrinkage of a unit cell was observed in CeCuOS, these materials, LnCuOS (Ln = Ce, Pr, and Nd), basically crystallize in the same crystal structure as that of LaCuOS. This observation suggests that LnCuOS (Ln = Ce, Pr, and Nd) may show electrical and optical properties similar to those of LaCuOS. However, it is also considered that 4f electrons in the lanthanide ions affect the electronic structure, and different electrical and optical properties appear in these materials. In this paper, we examine the influence of the lanthanide ions on the electrical and optical properties in a series of LnCuOS (Ln = La, Ce, Pr, and Nd), along with the observation of the electronic structures of LnCuOS by normal/inverse photoemission measurements.

2. Experiments

Sample Preparation. LnCuOS (Ln = La, Pr, and Nd) oxysulfides were synthesized by conventional solid-state reaction of starting materials of Ln_2O_2S and Cu_2S. The starting materials were stoichiometrically mixed and the mixed powders were pressed into disks. The disks were placed in evacuated silica tubes and heated at 800 °C for 6 h. In the case of CeCuOS, Ce_2O_2S cannot be used as a starting material because of its instability in air.[9] Therefore, CeCuOS was prepared by a two-step process, sulfurization and postannealing. Mixed powders of CeO_2 and Cu_2S (CeO_2:Cu_2S = 2:1) were sulfurized at 800 °C for 2 h in the flow of dilute H_2S gas,[10] and the product was subsequently annealed at 800 °C for 6 h in an evacuated silica tube. The details of the sample preparation were reported in a previous paper.[8] Acceptor doping was carried out to increase electrical conductivity by substituting Sr ions for Ln ions. All samples except for Sr-doped CeCuOS were confirmed to be respective single phases by X-ray diffraction measurements. The color of LnCuOS (Ln = La, Pr, and Nd) was light brown, while that of CeCuOS was black.

Thin films of LnCuOS (Ln = La, Pr, and Nd) were prepared by a radio frequency sputtering method using a respective sintered disk as a target. The films were first deposited on silica glass substrates in an Ar/H_2S atmosphere at room temperature.[10] Since the as-deposited films were amorphous, the films were crystallized by postannealing at 800 °C for 2 h in evacuated silica tubes. The thickness of the films was ≈150 nm. The preparation of the thin films was reported in detail elsewhere.[11,12]

Characterization. Electrical conductivities were measured by the four-probe method using bar-shaped samples cut out of sintered disks. Although the disks were pressed by a cold isostatic press before sintering, their apparent densities were ≈70% for nondoped samples and 80% for Sr-doped samples after sintering. Seebeck measurements were carried out at room temperature to determine carrier species.

Diffuse reflectance spectra for powdered samples and optical absorption spectra for thin film samples were measured using a conventional UV−vis spectrometer (Hitachi U4000) to examine fundamental optical properties. Photoluminescence (PL) spectra of disked samples were measured at room temperature using a PL measurement system with a CCD detector. The fourth-harmonic (266 nm) of a Nd:YAG laser with power density of 1 mJ cm^{-2} $pulse^{-1}$ was used as excitation in the PL measurement.

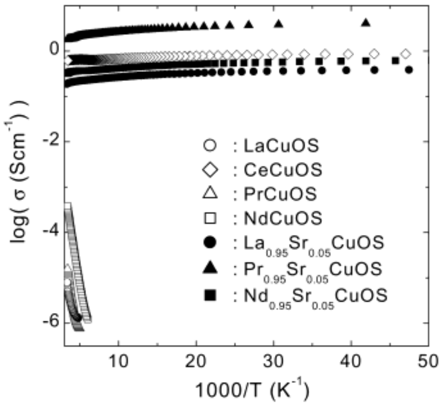

Figure 2. Electrical conductivities of nondoped and Sr-doped LnCuOS (Ln = La∼Nd) as a function of reciprocal temperatures.

Ultraviolet photoemission spectroscopy (UPS) measurements were conducted using the excitation lines of He II (40.8 eV). Inverse photoemission spectroscopy (IPES) measurements were carried out by detecting the photons of 9.5 eV emitted from samples. To obtain well-resolved spectra, highly conductive dense disks prepared by a spark plasma sintering system (Sumitomo Coal Mining Co.) were used as samples. The samples except for CeCuOS were doped with Sr 2 at. % to increase their electrical conductivities, and the apparent density of each sample was higher than 90%. The surfaces of the samples were scraped with a diamond file under the vacuum of 8×10^{-10} Torr to obtain clean surfaces before each measurement. The measurements of UPS and IPES spectra were performed in the pressure of 5×10^{-8} and 6×10^{-10} Torr, respectively. The Fermi energy (E_F) of Au was used for the calibration of the binding energy (E_B) in each spectrum.

3. Results and Discussion

Electrical Transport Properties. The electrical conductivities of the samples, LnCuOS (Ln = La, Ce, Pr, and Nd), are shown in Figure 2 against reciprocal temperatures. Nondoped samples of LnCuOS (Ln = La, Pr, and Nd) showed relatively low electrical conductivity and semiconducting behavior. Sr 5 at. % doped samples of LnCuOS (Ln = La, Pr, and Nd) exhibited much higher conductivity than the nondoped samples, and metallic or degenerate semiconducting behavior was observed. These results indicate that Sr ions at Ln ion sites effectively generate carriers in these materials. On the other hand, a nondoped sample of CeCuOS showed electrical conductivity as high as the Sr-doped LnCuOS (Ln = La, Pr, and Nd) and degenerate semiconducting behavior at low temperatures. This feature is unique to CeCuOS and probably related to the black color of this material. Seebeck coefficients of the samples are listed in Table 1, along with the electrical conductivities and energy gaps at room temperature. The Seebeck coefficients of all samples showed positive sign, indicating that holes are main carriers in these materials.

Optical Properties. The diffuse reflectance spectra of LnCuOS (Ln = La, Ce, Pr, and Nd) are shown in Figure 3. PrCuOS and NdCuOS showed reflectance spectra basically similar to that of LaCuOS, indicating that these oxysulfides have a wide energy gap of about

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Table 1. Electrical Conductivities (σ), Seebeck Coefficients (α), and Energy Gaps (E_g) of Nondoped and Sr-Doped LnCuOS (Ln = La~Nd) at Room Temperature.

samples	σ (S cm^{-1})	α (μV K^{-1})	E_g (eV)
LaCuOS	8.0×10^{-6}	+150	3.14
$La_{0.95}Sr_{0.05}CuOS$	0.19	+3	–
CeCuOS	0.61	+12	–
PrCuOS	1.6×10^{-5}	+340	3.03
$Pr_{0.95}Sr_{0.05}CuOS$	1.8	+9	–
NdCuOS	3.8×10^{-4}	+97	2.98
$Nd_{0.95}Sr_{0.05}CuOS$	0.32	+7	–

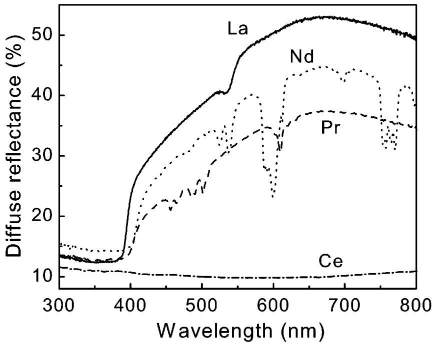

Figure 3. Diffuse reflectance spectra of LnCuOS (Ln = La~Nd) powders.

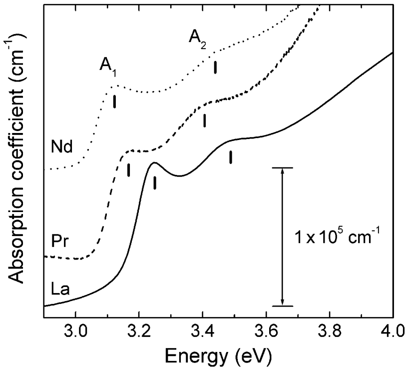

Figure 4. Optical absorption spectra of LnCuOS (Ln = La~Nd) thin films prepared by the sputtering method.

3 eV. Sharp absorption peaks observed in the spectra for PrCuOS and NdCuOS are due to f−f transitions intrinsic to respective lanthanide ions. This sharp absorption proves that 4f electrons in these materials are strongly localized and do not affect fundamental optical properties such as energy gaps. On the other hand, the diffuse reflectance of CeCuOS was rather low in the visible region, reflecting the black color of this material. These results suggest that the electronic structure of CeCuOS near the Fermi level is distinctly different from those of the other LnCuOS (Ln = La, Pr, and Nd).

The optical absorption spectra of the wide-gap samples, LnCuOS (Ln = La, Pr and Nd), are shown in Figure 4. A red shift of the absorption edges was observed in the series of LnCuOS (Ln = La, Pr, and Nd). The energy gaps were estimated from the plot of $(\alpha h\nu)^2 - h\nu$, where α, h, and ν are an absorption coefficient, Plank constant, and frequency, respectively. The values of the energy gaps are given in Table 1. The energy gaps become smaller as the atomic number of the lanthanide ions increases. The reduction of the ionic size due to the lanthanide contraction decreases the lattice constants of both *a* and *c* in these materials.[8] The decrease in the *a*-axis enhances the interaction between Cu ions within a $(Cu_2S_2)^{2-}$ layer and that in the *c*-axis results in narrower width of a $(Ln_2O_2)^{2+}$ layer and increases the interaction between the $(Cu_2S_2)^{2-}$ layers through the $(Ln_2O_2)^{2+}$ layers. These two consequences, especially the former one, are considered to drive the energy gap smaller in the series of LnCuOS (Ln = La, Pr, and Nd).

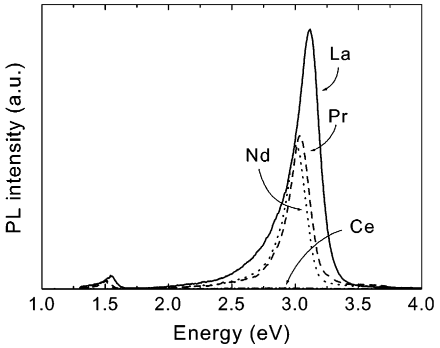

Figure 5. Photoluminescence spectra of LnCuOS (Ln = La~Nd) under excitation by 4ω (266 nm) of a Nd:YAG laser.

Another important observation in the absorption spectra of Figure 4 is that LnCuOS (Ln = La, Pr, and Nd) shows two absorption peaks of A_1 and A_2 near the absorption edge. These peaks in PrCuOS and NdCuOS are assigned to excitonic absorption as done in LaCuOS in our previous study.[3] This observation indicates that excitons are stable in these LnCuOS (Ln = La, Pr, and Nd) even at room temperature.

The PL spectra of LnCuOS (Ln = La, Ce, Pr, and Nd) are shown in Figure 5. PrCuOS and NdCuOS show sharp PL peaks around 3 eV in the manner similar to LaCuOS. This sharp PL peak in PrCuOS or NdCuOS is attributed to excitons as done in LaCuOS previously.[3] On the other hand, no PL peak was observed for CeCuOS in this energy region. These results in the PL measurements, as well as the diffuse reflectance measurements, indicate that the electronic structure of CeCuOS is unique among those of LnCuOS.

Since the conduction band and valence band of LaCuOS consist of a Cu 4s band and Cu 3d−S 3p hybridized band, respectively,[4] the excitons in LaCuOS generate in a $(Cu_2S_2)^{2-}$ layer sandwiched between $(La_2O_2)^{2+}$ layers. The optical absorption and PL spectra of PrCuOS and NdCuOS indicate that the excitons in these materials are also generated or recombine within a $(Cu_2S_2)^{2-}$ layer, irrespective of the presence of rare earth ions with open 4f shells. Since no photoluminescence originating from these lanthanide ions was observed, the 4f electrons do not influence the photoluminescence properties and energy transfer from the excitons to the 4f electrons does not occur sufficiently in these materials. In other words, it is considered that the excitons in LnCuOS (Ln = La, Pr, and Nd) are tightly confined within a $(Cu_2S_2)^{2-}$ layer by the barrier of $(Ln_2O_2)^{2+}$ layers.

Electronic Structures. The optical and electrical transport measurements revealed that only CeCuOS shows unique behavior among LnCuOS (Ln = La, Ce, Pr, and Nd): black color, no photoluminescence, and high electrical conductivity without doping. In addition, an anomalous shrinkage of the unit cell volume has been reported for CeCuOS.[7,8] To understand these unique properties of CeCuOS, the electronic structures of

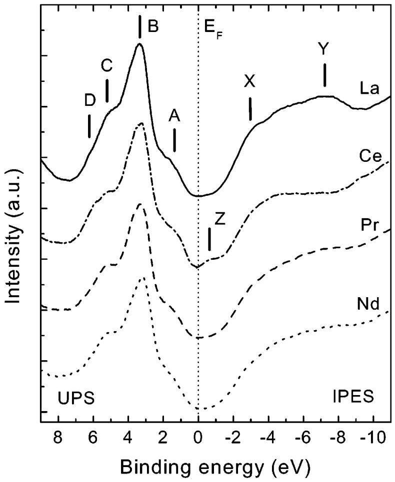

Figure 6. UPS and IPES spectra of LnCuOS (Ln = La~Nd). UPS and IPES spectra of each sample were combined at E_F ($E_B = 0$ eV).

LnCuOS (Ln = La, Ce, Pr, and Nd) were observed by the UPS and IPES measurements.

Figure 6 shows the UPS and IPES spectra of LnCuOS (Ln = La, Ce, Pr, and Nd). In our previous study,[4] the electronic structure of LaCuOS, a prototype of LnCuOS, was observed, and four peaks, peak A to D, in the valence band and two peaks, peak X and Y, in the conduction band were found as indicated in Figure 6. On the basis of the energy band calculations, the four peaks in the valence band were assigned to the Cu 3d−S 3p hybridized band for peak A, the Cu 3d band for B, the S 3p band for C, and the O 2p band for D. The two peaks in the conduction band were assigned to the La 5d−Cu 4s band for peak X and the La 5d−Cu 4p band for Y. Since LaCuOS is a wide-gap p-type semiconductor, the Fermi level is located at the top of the valence band and a wide energy gap is seen above the Fermi level. The shape of the spectra for PrCuOS and NdCuOS is almost the same as that for LaCuOS. These observations suggest that the electronic structures of PrCuOS and NdCuOS are analogous to that of LaCuOS except for the 4f bands, and this is the origin of the similar optical and electrical transport properties among LnCuOS (Ln = La, Pr, and Nd).

In the case of CeCuOS, remarkable differences were found in the structure of the conduction bands, although the structure of the valence band is rather similar to those of LnCuOS (Ln = La, Pr, and Nd). In the IPES spectrum of CeCuOS, the intensity of peak Y significantly decreases and peak Z indicated in Figure 6 appears near the Fermi level. Since peak Z is located at the middle of the band gap for LnCuOS (Ln = La, Pr, and Nd), it is reasonable for CeCuOS to give black color and no photoluminescence. Although Ce 4f or 5d orbitals are probably the main components of the band for peak Z, it is hard, so far, to elucidate clearly which orbitals are responsible for peak Z in the IPES spectrum. CeCuOS exhibits higher electrical conductivity than the other LnCuOS (Ln = La, Pr, and Nd). However, the Fermi edge was not observed clearly in the UPS and IPES measurements. This is probably because carrier concentration is not as high as the usual metals. Therefore, we tentatively consider that CeCuOS is in a semimetallic state. The observation of the electronic structure of CeCuOS revealed that the presence of an unoccupied band near the Fermi level causes the unique optical and electrical transport properties of CeCuOS.

4. Conclusion

The electrical and optical properties were examined in the series of LnCuOS (Ln = La~Nd). We found that LnCuOS (Ln = La, Pr, and Nd) are wide-gap p-type semiconductors with excitonic absorption and emission features, while CeCuOS is exceptionally a degenerate semiconductor in a semimetallic state. The absorption due to f−f transitions and the excitonic absorption/emission in PrCuOS and NdCuOS demonstrated that the 4f electrons in these lanthanide ions are localized without the influence on the fundamental optical properties and no significant energy transfer occurs between excitons in $(Cu_2S_2)^{2-}$ layers and the lanthanide ions in $(Ln_2O_2)^{2+}$ layers. The electronic structures of LnCuOS (Ln = La~Nd) were observed by the UPS and IPES measurements to understand their electrical and optical properties. The wide energy gap and the position of the Fermi level observed commonly in LnCuOS (Ln = La, Pr, and Nd) proved directly that these oxysulfides are wide-gap p-type semiconductors. On the other hand, an unoccupied band was observed near the Fermi level in CeCuOS, and the unique electrical and optical properties of CeCuOS are considered to originate from this unoccupied band.

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