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Electrical properties of layered copper oxyselenides $(BiO)Cu_{1-x}Se$ and $(Bi_{1-x}Sr_x)OCuSe$

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Abstract

Electrical resistivity (ρ), Hall coefficient (R_H), and Seebeck coefficient (S) measurements were performed on carrier-doped oxyselenide samples $(BiO)Cu_{1-x}Se$ ($0 \leq x \leq 0.020$) and $(Bi_{1-x}Sr_x)OCuSe$ ($0 \leq x \leq 0.10$). $(BiO)Cu_{1-x}Se$ showed a first order phase transition at ~ 250 K, which is characterized by a broad maximum of the $\rho - T$ curves. Hall measurements revealed that the samples are degenerate semiconductors. On the basis of R_H and S measurements, the conduction is supposed to be of the two-carrier type, while the dominant carriers are holes mainly originating from the Cu deficiency. The samples of $(Bi_{1-x}Sr_x)OCuSe$ showed results similar to those of $(BiO)Cu_{1-x}Se$, although a two-type-carrier conduction was not observed.

Keywords: Carrier doped (BiO)CuSe; Electrical resistivity; Hall coefficient; Degenerate semiconductor; Phase transition

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1. Introduction

Multinary oxysulfide (LaO)CuS was first reported by Palazzi et al. [1,2]. This compound has a (LaO)AgS-type structure with space group *P4/nmm* [3,4]. (LaO)CuS was found to be a p-type semiconductor by Ishikawa et al. [5]. The present authors prepared a large number of isostructural compounds (LnO)CuSe (Ln = La, Ce, Nd, Sm, Gd, Tb, Dy, Ho, Y), and found that $(La_{0.80}Sr_{0.20})OCuSe$ exhibits a metal-to-semiconductor transition at ~ 100 K [6]. Recently, Kusainova et al. [7] and Berdonosov et al. [8] prepared the new isostructural chalcogenides (BiO)CuS and (BiO)CuSe, in addition to (MO)CuSe (M = Nd, Gd, Dy). A schematic structure of (BiO)CuSe is shown in Fig. 1. The structure is constructed from alternating (Cu_2Se_2) layers and (Bi_2O_2) fluorite-like layers, where the (Cu_2Se_2) layers consist of slightly distorted $CuSe_4$ tetrahedra with shared Se–Se edges, and the (Bi_2O_2) layers consist of slightly distorted Bi_4O tetrahedra with shared Bi–Bi edges [7]. These compounds are all semiconducting. In the present study we have investigated the electrical properties (electrical resistivity, Hall coefficients, and Seebeck coefficients) of the carrier-doped samples of the $(BiO)Cu_{1-x}Se$ system and the $(Bi_{1-x}Sr_x)OCuSe$ system.

2. Experimental

The samples of $(BiO)Cu_{1-x}Se$ were prepared by heating the appropriate ratios of the mixtures of Bi, Bi_2O_3, Cu, and Se in evacuated silica tubes at 400°C for 1 week. After grinding and pelletizing, the samples were sintered at 400°C for 1 further week. The samples of $(Bi_{1-x}Sr_x)OCuSe$ were prepared in the same manner from the mixtures of Bi, Bi_2O_3, Cu, Se, and

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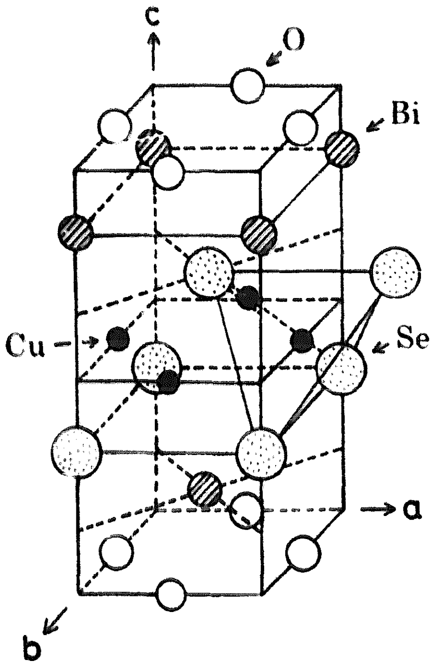

Fig. 1. Schematic drawing of the structure of (BiO)CuSe (space group $P4/nmm$).

SrO. Obtained samples were identified by powder X-ray diffraction measurements using a RIGAKU RAD-B. Differential scanning calorimetry (DSC) measurements were performed with a MAC SCIENCE DSC-3100. Electrical resistivity ρ measurements were carried out for powdered pellets with an ordinary dc four-probe method from 2 to 300 K. Resistivity of (BiO)$Cu_{0.985}$Se was measured down to 20 mK using a $^3He-^4He$ dilution refrigerator. Hall coefficients (R_H) were measured for powdered thin pellets by a dc five-probe method from 77 to 300 K under the following conditions: thickness of the samples, 0.2–0.3 mm; applied magnetic field, 1 Tesla; and current, 10 mA. Thermoelectric power (Seebeck coefficients, S) measurements were performed for (BiO)$Cu_{0.980}$Se from 115 to 300 K, using Cu leads with a temperature gradient of 3–4 K.

3. Results and discussion

3.1. The (BiO)Cu_{1-x}Se system

X-ray diffraction studies revealed that (BiO)Cu_{1-x}Se is stable in the composition range $0 \leq x \leq 0.02$. Temperature variations of the resistivity ρ of (BiO)Cu_{1-x}Se ($0 \leq x \leq 0.020$) are shown in Fig. 2, and the enlarged $\rho - T$ curve of (BiO)$Cu_{0.980}$Se is shown in Fig. 3. The values of ρ decrease as the Cu content decreases, indicating that the carriers originate from the Cu deficiency. The $\rho - T$ curve of a stoichiometric sample of (BiO)CuSe shows a semiconductive behavior exhibiting a broad maximum around 250 K.

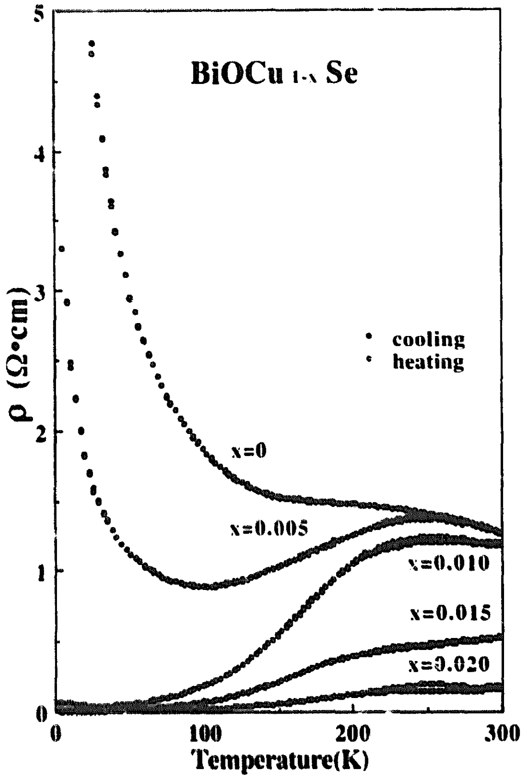

Fig. 2. Temperature variations of the electrical resistivity ρ of (BiO)Cu_{1-x}Se from 2 to 300 K.

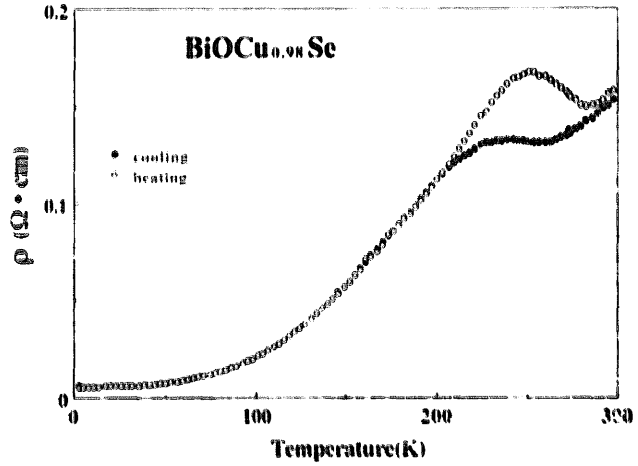

Fig. 3. Temperature dependence of the electrical resistivity ρ of (BiO)$Cu_{0.980}$Se from 2 to 300 K.

The nonstoichiometric samples also show the broad maximum at ~ 250 K, accompanying a small hysteresis. The hysteresis is most obviously observed in (BiO)$Cu_{0.980}$Se, as shown in Fig. 3. A small latent heat was observed at ~ 250 K for all samples in the DSC measurements. The latent heat, as well as the hysteresis observed at the anomaly temperature, suggests that the compound has a first order phase transition at ~ 250 K.

It is of interest that (BiO)Cu_{1-x}Se possesses some aspects common to a bismuth copper oxide superconductor, i.e. both materials have two-dimensionality, and both contain elements Bi, Cu, and O. We may expect superconductivity in the conductive samples of (BiO)Cu_{1-x}Se. Fig. 4 shows the temperature dependence of ρ for (BiO)$Cu_{0.985}$Se measured on cooling from 2000 to 20 mK. The resistivity of (BiO)$Cu_{0.985}$Se gradually increases with decreasing temperature, exhibiting no superconductivity.

Fig. 5 shows the temperature variations of the Hall coefficient R_H for (BiO)Cu_{1-x}Se ($0 \leq x \leq 0.020$) observed on cooling. The results on heating were consistent with those in the cooling runs. The Hall coefficients for the samples of $x \leq 0.015$ are positive in the measured temperature range, indicating that the dominant carriers are the holes. The decreasing tendency of R_H with increasing temperature indicates that the samples are semiconductors rather than metals. Contrary to the ρ measurements, the Hall measurements show no anomalous behavior at the transition temperature. The holes are considered to be supplied to the energy band (presumably to the selenium p bands) to compensate for the lack of total positive charges induced by the Cu deficiency. This speculation is based on the experimental results of an X-ray photoelectron spectroscopy (XPS) study by Folmer and Jellinek, which confirmed that the Cu atoms are in the monovalent state in many copper chalcogenides [9].

Fig. 6 shows the temperature variations for the hole concentrations n of (BiO)Cu_{1-x}Se ($0 \leq x \leq 0.020$), which are derived from the Hall data by adopting the one carrier model $R_H = +1/ne_0$, where e_0 is the electronic charge. The number of n shows only slight variations with temperature below ~200 K, indicating that the samples are degenerate semiconductors. The large carrier numbers of 10^{18}–10^{20} cm^{-3} are also in agreement with the degenerate nature. Assuming that the deficient copper atoms x produce just the same number of holes, then the hole densities are calculated to be 7.25×10^{19}, 1.46×10^{20}, 2.17×10^{20}, and 2.89×10^{20} cm^{-3}, respectively for the samples of x = 0.05, 0.010, 0.015, and 0.020. For each sample, the observed hole densities (at 298 K) are smaller than those of the calculated ones by an order of magnitude of approximately 10. This discrepancy may originate from a small part of the Cu atoms which are oxidized to the divalent state in the Cu deficient samples. This may be acceptable because the present compound would have the bonding nature of the oxide as well as the chalcogenide. Another plausible origin for the discrepancy could be that the measuring temperatures are not sufficiently high enough as to supply the ample number of holes. The energy band calculations as well as the XPS measurements are needed to clarify these problems. The somewhat large concentration of holes observed in (BiO)CuSe may indicate that a small number of Cu vacancies remain even in the stoichiometric sample.

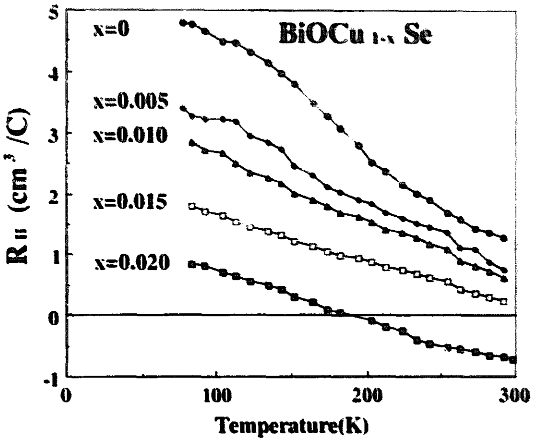

Fig. 5. Temperature variations of the Hall coefficient R_H of (BiO)Cu_{1-x}Se measured on cooling. Solid lines are guides to the eye.

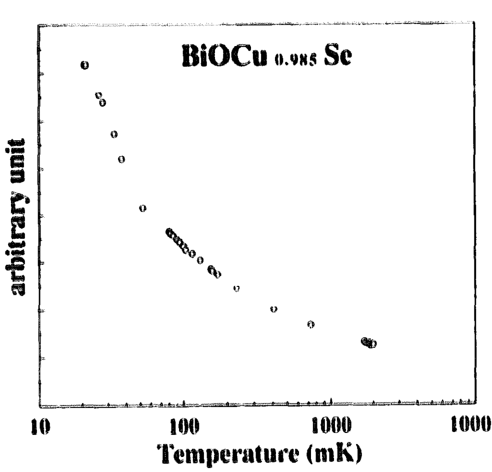

Fig. 4. Temperature dependence of the electrical resistivity ρ of (BiO)$Cu_{0.985}$Se measured on cooling from 2000 to 20 mK.

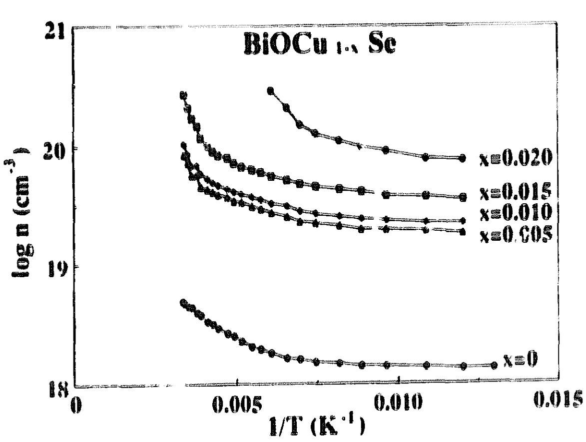

Fig. 6. Temperature variations of the hole concentration n of (BiO)Cu_{1-x}Se. Solid lines are guides to the eye.

Fig. 7 shows the temperature variations of the Hall mobility μ ($=R_H \cdot \sigma$) for (BiO)Cu$_{1-x}$Se ($0 \leq x \leq 0.020$), where σ denotes the conductivity. The rather small values of μ imply that there are many scattering factors in the samples, i.e. vacancies, impurities, dislocations, grain boundaries, etc. The mobility shows a near $T^{-2/3}$ dependence above ~ 200 K for samples with $x \leq 0.015$, indicating that the lattice scattering is dominant in this temperature range.

It is noticed that (BiO)Cu$_{0.980}$Se shows the negative values of R_H above ~ 180 K, indicating that the dominant carriers are electrons in this temperature range. This behavior could be explained by a two-carrier model. For the two-type-carrier conduction, the Hall coefficient is given by the formula,

$$R_H = 3\pi(p\mu_h^2 - n\mu_e^2)/[8e(p\mu_h + n\mu_e)]^2, \qquad (1)$$

where p and n are the densities of the hole and the electron, respectively, and μ_h, μ_e are the corresponding mobilities. The negative values of R_H are expected to be observed when the term $n\mu_e^2$ is larger than $p\mu_h^2$. Such a situation would occur in the case when the compound is a semiconductor with a many-valley band structure, where the electrons are transported in a rather wide conduction band which allows for a large mobility. The presence of donor levels may be a possible origin of the mixed conduction. In the present case, however, we can hardly assume the existence of a large amount of impurities, or other factors responsible for the electron donation.

To investigate the conduction mechanism in more detail, we have performed Seebeck measurements. The temperature dependence of the Seebeck coefficient, S for (BiO)Cu$_{0.980}$Se is shown in Fig. 8. The distinct anomaly observed at 200–260 K must surely correspond to the transition observed in the ρ measurements. The positive values of S indicate that the dominant carriers are holes in the measured temperature range, which seems to contradict with the results of the Hall measurements. In the case of two overlapping bands of standard form, one obtains

$$S = (\sigma_h S_h + \sigma_e S_e)/(\sigma_h/\sigma_e), \qquad (2)$$

where σ_h, σ_e, and S_h, S_e, are the values of σ and S if only one band is present [10]. Incorporating the present results for the measurements of S to Eq. (2), the absolute values of S_e are expected to be smaller than those of S_h. This suggests that the conduction of electrons has a metallic nature, exhibiting rather small values of S, which seems to be in accord with the expectation of a wide band conduction for the electrons as discussed above. The other compositional samples of (BiO)Cu$_{1-x}$S show almost T-linear dependences of R_H similar to (BiO)Cu$_{0.980}$Se, and thus the values of R_H seem to become negative at higher temperatures, suggesting that a mixed conduction is also apparent for all Cu deficient samples.

The origin of the phase transition is not clear. The possible candidates could be a structural change, such as an order–disorder transition, a semiconductor–metal transition originating from the strong electron correlation, a charge–density-wave transition caused by the electron–lattice interaction, etc. One may consider the possibility that the transition is intrinsic to an impurity phase possibly existing in the samples of $x \leq 0.02$, which cannot be detected in the X-ray measurements. This possibility, however, can be excluded by the following observations which show that the system is homogeneous in the range $0 \leq x \leq 0.02$, i.e. the latent heat was not enhanced as the Cu content was decreased, and the Hall measurements showed that the carrier concentration was almost constant when x increased beyond 0.02.

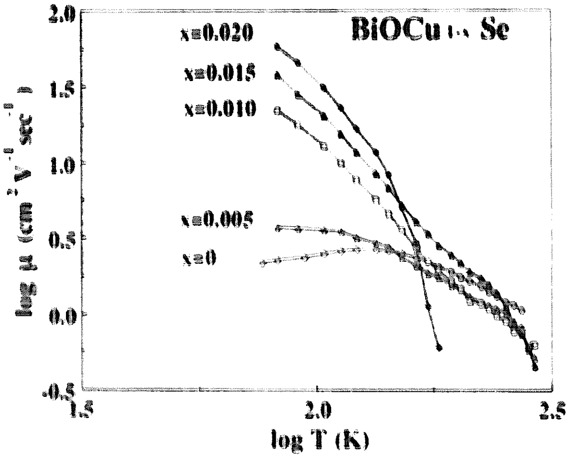

Fig. 7. Temperature variations of the Hall mobility μ ($=R_H \cdot \sigma$) of (BiO)Cu$_{1-x}$Se. Solid lines are guides to the eye.

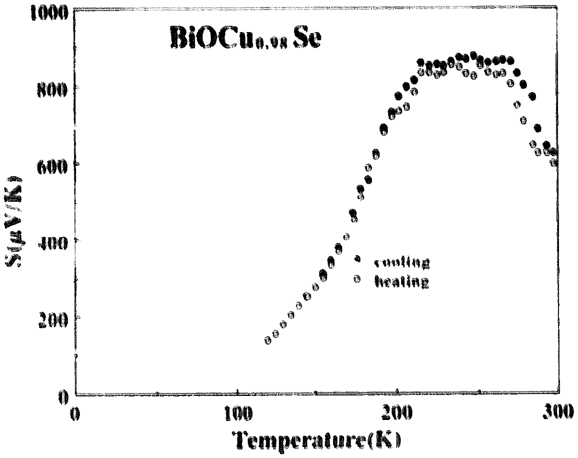

Fig. 8. Temperature dependence of the Seebeck coefficient S of (BiO)Cu$_{0.980}$Se.

3.2. The $(Bi_{1-x}Sr_x)OCuSe$ system

The X-ray diffraction studies revealed that $(Bi_{1-x}Sr_x)OCuSe$ is stable in the range $0 \le x \le 0.10$. The temperature variations of ρ of $(Bi_{1-x}Sr_x)OCuSe$ $(0 \le x \le 0.10)$ are shown in Fig. 9. The transition is more gradual compared with that observed in the Cu deficient system. Fig. 10 gives the temperature variations of R_H of $(Bi_{1-x}Sr_x)OCuSe$ $(0 \le x \le 0.10)$, which were measured on cooling from 300 to 77 K. The dominant carriers are the holes in the measured temperature range for all samples. The holes are considered to be introduced by the substitution of Sr^{2+} for Bi^{3+}. The observed hole densities were smaller than the calculated ones by on order of magnitude of approximately 10 for all samples, which is quite similar to the results of the $(BiO)Cu_{1-x}Se$ system. The Hall mobility seems to show a $T^{-2/3}$ dependence above ~ 200 K, which is also similar to the results of the $(BiO)Cu_{1-x}Se$ system. This system exhibits no evidence for the two-type-carrier conduction, which may suggest that the conduction is carried in the different energy bands from those in the Cu deficient samples.

4. Conclusions

The Hall measurements showed that carrier-doped samples of $(BiO)Cu_{1-x}Se$ $(0 \le x \le 0.020)$ are degenerate semiconductors. Although the dominant carriers are holes mainly originating from the deficiency of Cu atoms, conduction is possibly carried by two carriers, to which a many-valley band model was proposed.

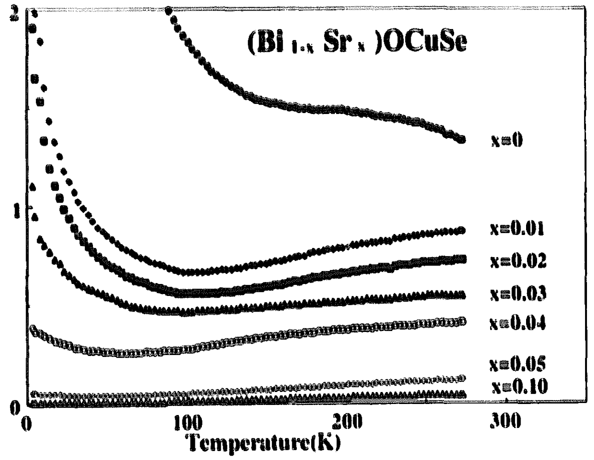

Fig. 9. Temperature variations of the electrical resistivity ρ of $(Bi_{1-x}Sr_x)OCuSe$ measured on cooling from 300 to 2 K.

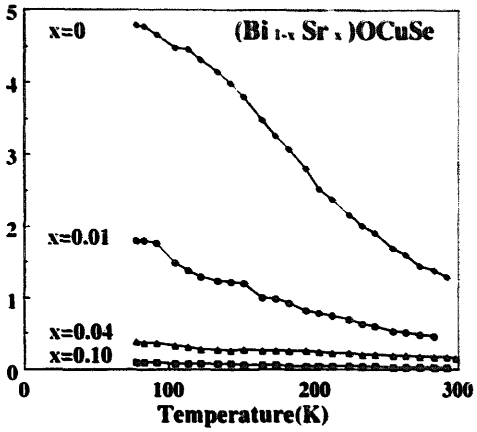

Fig. 10. Temperature variations of the Hall coefficient R_H of $(Bi_{1-x}Sr_x)OCuSe$ measured on cooling. Solid lines are guides to the eye.

From the results of the Hall and Seebeck measurements, it is supposed that a rather wide conduction band is responsible for the electron conduction. A band calculation is needed to clarify this speculation. The origin of the transition should also be clarified. For this purpose, both X-ray and electron microscopy investigations are now in progress. The system $(Bi_{1-x}Sr_x)OCuSe$ $(0 \le x \le 0.10)$ showed results substantially identical to those of the $(BiO)Cu_{1-x}Se$ system, although a two-type-carrier conduction was not observed.

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