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Electrical properties and phase transitions of $TlCu_3S_2$ and $BaCu_2S_2$

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Abstract

$TlCu_{3-x}S_2$ showed a phase transition at ~100 K, which is characterized by a jump of the resistivity and a steep increase of the Hall coefficient on cooling. The dominant carriers were observed to be holes in the measurements of Seebeck coefficients (S) and Hall coefficients (R_H). The holes were found to originate mainly from copper vacancies. The Hall mobility scarcely changed at the transition temperature. α-$BaCu_{2-x}S_2$ showed semiconductive behaviors with fairly large values of S, and exhibited a phase transition at ~200 K. β-$BaCu_{2-x}S_2$ was a semiconductor, exhibiting a phase transition at ca. 250 K. S and R_H measurements showed that the dominant carriers are holes in both α and β phases.

Keywords: Ternary copper sulfide; Phase transition; Resistivity; Thermopower; Hall coefficient

1. Introduction

Ternary copper chalcogenides exhibit a large variety of phase transitions. $K_3Cu_8S_6$ was reported to show CDW (charge density wave)-like transitions at 55 and 153 K [1–4]. We found successive phase transitions at 60, 165, 190, 220, 245 and 395 K in quasi-one-dimensional sulfide, $TlCu_{7-x}S_4$ [5,6]. Superlattice modulations were observed at 165 and 245 K in electron diffraction patterns. Isotypic sulfides of $KCu_{7-x}S_4$ and $RbCu_{7-x}S_4$ showed similar behaviors [5,6]. We also found α-$BaCu_{4-x}S_3$ to show a phase transition at ~190 K [7]. On the basis of extended Hückel tight-binding band calculations, Whangbo and his coworkers claimed that the phase transitions of $K_3Cu_8S_6$ and ACu_7S_4 (A=Tl, K, Rb) cannot originate from the CDW instability, but are caused by an ordering of copper atoms [8,9].

$TlCu_3S_2$ has a monoclinic structure of a $CsAg_3S_2$-type with space group $C2/m$ [10]. The structure is composed with infinite $[Cu_4S_4]$ columns running along the b axis, where copper atoms in $[Cu_4S_4]$ columns are coordinated triangularly. The columns are bridged by edge-shared CuS_4 tetrahedral chains to form Cu_3S_2 layers parallel to the ab plane. The layers are separated from each other by the intercalated Tl atoms coordinated by seven S atoms. $BaCu_2S_2$ occurs in two phases α and β; the α phase has an orthorhombic structure with space group $Pnma$ [11,12], and the β phase a tetragonal structure with space group I_4/mmm [13,14]. The structure of the α phase is constructed by the infinite tubes which are formed by sharing the basal faces of trigonal prisms of anions containing Ba at the center. The tubes make up corrugated sheets by sharing two edges with neighboring tubes to form tetrahedral holes which are occupied by copper atoms (Cu2). The Cu2 atoms constitute zigzag chains of CuS_4 tetrahedra, which are formed by sharing two adjacent edges of each tetrahedron. The β-$BaCu_2S_2$ adopts a $ThCr_2Si_2$-type structure with Cu_2S_2 layers separated by Ba sheets. Each Cu_2S_2 layer is made of edge-sharing CuS_4 tetrahedra to form anti-PbO-type structure. Very recently, Huster and Bronger prepared the single crystals of both α and β phases, and found the α–β transition at 813 (±10) K in high-temperature XRD measurements [15]

Sato and Kojima reported that KCu_3S_2, which is isostructural with $TlCu_3S_2$, showed a metallic conduction along the b axis [16,17]. Seebeck measurements also showed the metallic conduction with holes as the dominant carriers [17]. They claimed that the metallic behavior of this compound would originate from the nonstoichiometry. Ouammou et al. observed that β-$BaCu_2S_2$ exhibited semiconductive behavior [18]. Zhang et al. reported that β-$K_xBa_{1-x}Cu_2S_2$ (x=0.2, 0.35) shows a p-type metallic conduction [19].

In the present work, we performed electrical resistivity, thermoelectric power, and Hall measurements on $TlCu_{3-x}S_2$, and on α- and β-$BaCu_{2-x}S_2$.

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2. Experimental

$TlCu_{3-x}S_2$ was prepared as follows. The desired ratios of elemental mixtures of Tl, Cu and S were sealed in evacuated silica tubes. The starting mixtures were gradually heated to 673 K, and were annealed at this temperature for 21 days. After grinding and pelletization, the products were sintered in sealed silica tubes at 573 K for 14 days, and then were slowly cooled to room temperature. $BaCu_{2-x}S_2$ was prepared as follows. Elemental mixtures with desired ratios were sealed in evacuated silica tubes. To prevent the reaction of barium with silica, the inside of silica tubes was coated with thin carbon films by means of pyrolysis of acetone. The mixtures were gradually heated to 1073 K, and were annealed at this temperature for 5 days. The products were pelletized and sealed in silica tubes, followed by annealing at 873 K for 3 days. The α phase was obtained by slowly cooling to room temperature, and the β phase by quenching from 873 K to water. All samples were analyzed by powder X-ray diffraction (XRD) method with CuKα radiation using Rigaku Rint-2500. Differential thermal analysis (DTA) measurements were carried out for both $TlCu_{3-x}S_2$ and $BaCu_{2-x}S_2$ from room temperature to 1073 K with a heating–cooling rate of 10 K min^{-1} using Mac Science TG-DTA 2000, where samples were sealed in small silica capsules with thin flat bottom specially designed for DTA measurements. Differential scanning calorimetry (DSC) measurements were carried out for both sulfides from 110 to 273 K using Mac Science DSC-3100 with a cooling–heating rate of 10 K min^{-1}. Electrical resistivity (ρ) measurements were performed by an ordinary dc four probe method down to 2 K. Thermoelectric power (Seebeck coefficient, S) was measured from 90 to 273 K using copper leads with a temperature gradient of ca. 0.3 K cm^{-1}. In both ρ and S measurements copper leads were contacted with sintered pellets by gold paste. Measurements of Hall coefficients (R_H) were performed on powdered thin pellets using a dc five-probe method from 77 to 273 K under the following conditions: thickness of the samples, 0.2–0.4 mm; applied magnetic field, 1 Tesla; and currents, 100 mA for $TlCu_{3-x}S_2$ and 10 mA for $BaCu_{2-x}S_2$.

3. Results and discussion

3.1. Electrical properties and a phase transition of $TlCu_{3-x}S_2$

It was found in XRD measurements that $TlCu_{3-x}S_2$ is stable in the composition range of $x \leqq 0.05$. XRD patterns of samples of $x \geqq 0.07$ showed a few unknown peaks. Lattice parameters of $TlCu_3S_2$ were $a=1.462$ nm, $b=0.3877$ nm, $c=0.8298$ nm, and $\beta=111.8°$, which are well identical with those reported by Klepp and Yvon [10]. DTA measurements of $TlCu_3S_2$ showed endothermic peaks at 692, 806 and 923 K on heating, and exothermic peaks at 680, 770 and 897 K on cooling, where the peaks observed at 692 and 680 K were most pronounced in heating and cooling runs, respectively. These results suggest that this compound melts incongruently at 680–692 K.

Fig. 1 shows temperature variations of ρ of $TlCu_{3-x}S_2$ ($x=0$, 0.05, 0.07, and 0.09) measured on cooling. Observations were all reversible in cooling and heating runs. In cooling measurements $TlCu_3S_2$ showed a small jump of ρ at ~220 K and then exhibited a sharp increase of ρ below ~100 K. The sample of $x=0.05$ also showed a large increase of ρ below ~100 K. The resistivity increased by about 10 times from 100 to 60 K in both samples. Samples of $x=0.07$ and 0.09 also showed similar behaviors, although these samples contained a small amount of unknown phase(s). These observations clearly indicate that $TlCu_{3-x}S_2$ has a phase transition at around 100 K. DSC measurements showed no detectable latent heat at the transition temperature. Fig. 2 shows temperature dependences of S for $TlCu_{3-x}S_2$ ($x=0$, 0.05, 0.07, and 0.09). Rather large values of S for $x=0$ and 0.05 indicate that both samples are semiconductors. The values of S for all samples were positive in the measured temperature range, indicative of hole conduction.

Fig. 3 shows temperature variations of Hall coefficients (R_H) of $TlCu_{3-x}S_2$ ($x=0$, 0.05), where the solid lines are guides to the eye. The positive values of R_H indicate the hole conduction, compatible with the Seebeck measure-

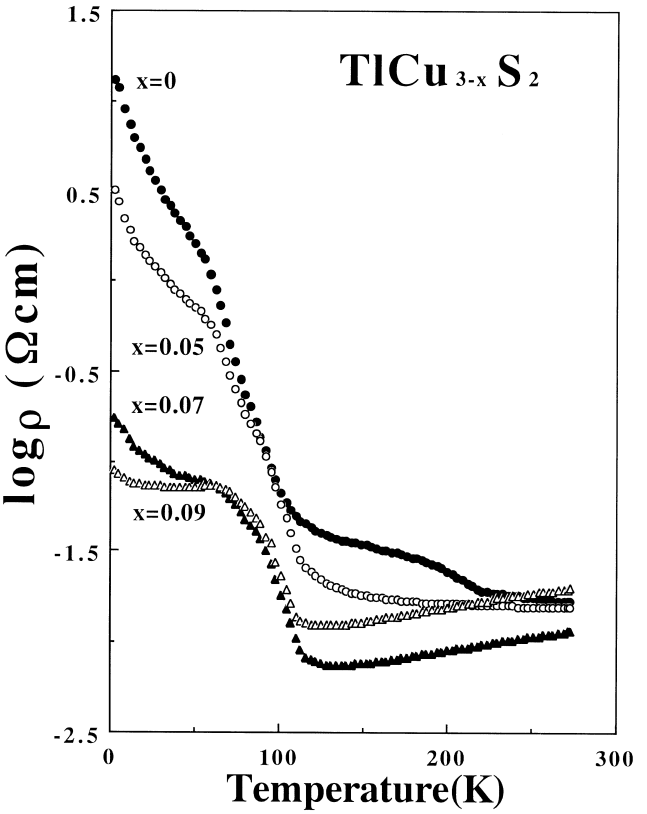

Fig. 1. Temperature variations of electrical resistivity ρ of $TlCu_{3-x}S_2$ ($x=0$, 0.05, 0.07 and 0.09).

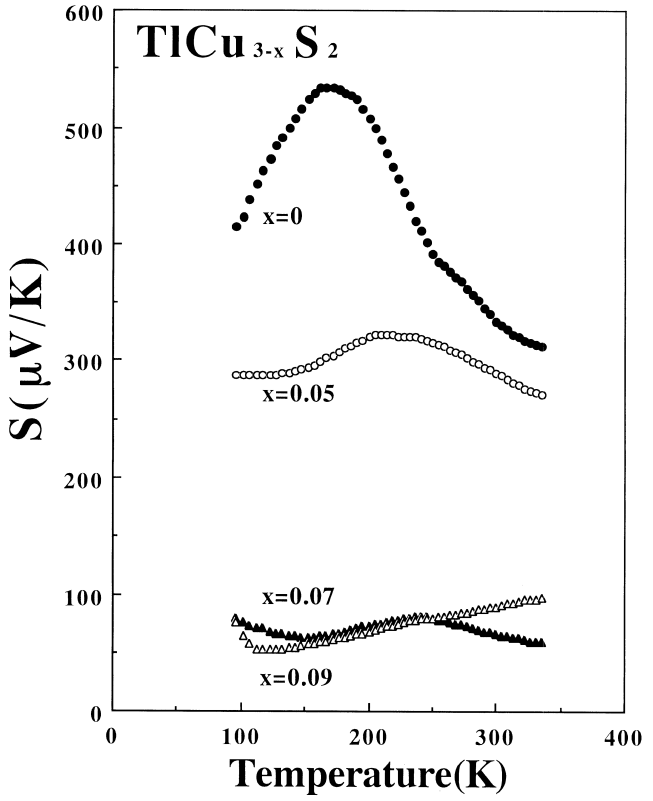

Fig. 2. Temperature variations of Seebeck coefficients S of $TlCu_{3-x}S_2$ ($x=0$, 0.05, 0.07 and 0.09).

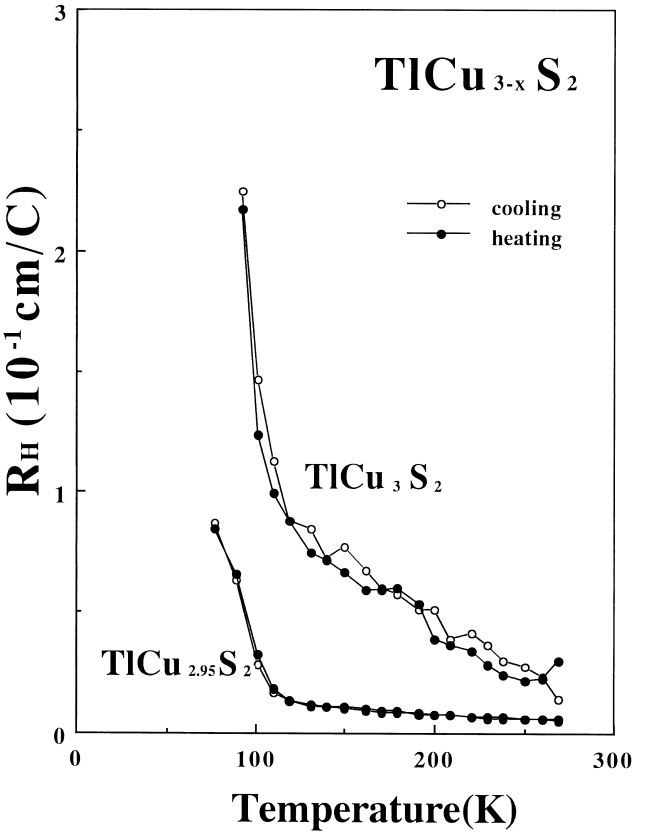

Fig. 3. Temperature variations of Hall coefficients R_H of $TlCu_{3-x}S_2$ ($x=0$ and 0.05). Solid lines are guides to the eye.

ments. The values of R_H showed a sharp increase below ~100 K, corresponding to the transition. Fig. 4 shows temperature dependences of the hole concentrations n for $TlCu_{3-x}S_2$ ($x=0$, 0.05, and 0.09), which were derived from Hall data by adopting the simple one carrier model $R_H=+1/ne_0$, where e_0 is the electron charge. The results clearly indicate that the sharp increase of ρ below 100 K is associated with a sharp decrease of the hole density. This compound should be a semiconductor, because the formal oxidation state of copper in most binary and ternary copper chalcogenides is Cu^+ [20], and the sulfur is also in the closed shell oxidation state of S^{2-}. The holes, therefore, are expected to originate from the copper vacancies. Assuming that the deficient copper atoms x produce just the same number of holes, then the hole densities were calculated to be 4.58×10^{20} and 8.25×10^{20} cm^{-3} for the samples of $x=0.05$ and 0.09, respectively. The calculated values of n are near the values observed at ~100 K for these samples, indicating that the copper vacancies are most likely responsible for the hole conduction. For these samples, however, observed densities are somewhat larger than calculated ones above ~100 K, and are smaller below ~100 K, indicating that the conduction mechanism of this compound cannot be explained merely by the simple band model. On the basis of the observed hole densities, the copper composition x was roughly estimated to be 0.006 for the stoichiometric sample of $TlCu_3S_2$.

Fig. 5 gives temperature variations of the Hall mobility μ ($=R_H\cdot\sigma$) of $TlCu_{3-x}S_2$ ($x=0$, 0.05 and 0.09), where σ denotes the conductivity. Rather small values of μ suggest that the samples contain a lot of scattering factors such as vacancies, dislocations, grain boundaries, etc. The decreasing tendency of μ with increasing x suggests that the vacancies are the main factor for the scattering. The values of μ of the samples of $x=0$ and 0.05 scarcely changed with temperature, indicative of degenerate semiconductors. The values of μ showed no remarkable change at the transition temperature, indicating that the energy band structure does not significantly vary at this temperature. This result suggests that the CDW instability usually accompanied by superlattice formations may not be responsible for the transition. The most promising candidate for the origin of the transition would be an electron correlation effect, which occasionally causes the Mott transition. In order to see the origin of the transition more clearly, the crystal data below the transition temperature are needed.

3.2. Phase stability of α- and β-$BaCu_{2-x}S_2$

DTA measurements on $BaCu_2S_2$ showed an endothermic peak at 800 K on heating, and an exothermic peak at 772 K on cooling. These peaks can be attributed to the orthorhombic-to-tetragonal (α–β) transition. The transition temperature is quite consistent with that observed by

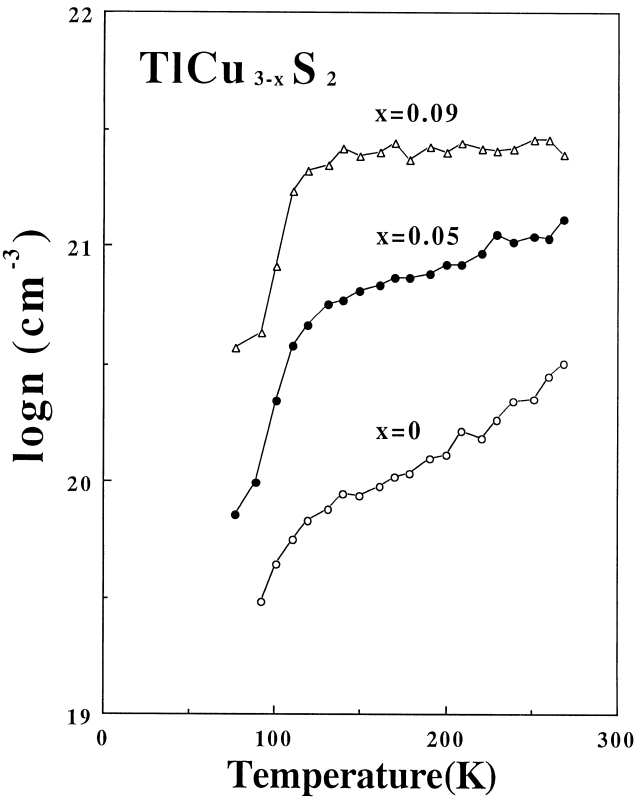

Fig. 4. Temperature variations of hole concentration n of $TlCu_{3-x}S_2$ ($x=0$, 0.05 and 0.09). Solid lines are guides to the eye.

Huster and Bronger in high-temperature XRD measurements [15]. The α-$BaCu_{2-x}S_2$ was observed to be stable in the composition range of $0 \leqq x \leqq 0.12$. Lattice parameters of α-$BaCu_2S_2$ were $a=0.9280$ nm, $b=0.4055$ nm, and $c=1.039$ nm, which are well consistent with the results of Iglesias et al. [11] and Huster and Bronger [15]. The parameters scarcely varied with the copper composition. The β-$BaCu_{2-x}S_2$ was observed to be stable in the range of $0 \leqq x \leqq 0.20$. The lattice parameters of β-$BaCu_2S_2$ were $a=0.3910$ nm and $c=1.265$ nm, which are compatible with those of Saeki and Onoda and co-workers [13,14] and Huster and Bronger [15]. Both parameters slightly decreased with increasing x.

3.3. Electrical properties of α-$BaCu_{2-x}S_2$

Fig. 6 gives temperature variations of ρ of α-$BaCu_{2-x}S_2$ ($x=0$, 0.05 and 0.12). All samples showed a transition at ~200 K, where the temperature dependences of ρ varied from metallic to semiconductive with lowering temperature. The energy gap in the temperature range between 70 and 150 K was estimated to be 0.061, 0.053 and 0.034 eV respectively for the samples of $x=0$, 0.05 and 0.12. Fig. 7 shows temperature dependences of S for α-$BaCu_{2-x}S_2$ ($x=0$, 0.05 and 0.12). The values of S are fairly large as compared with the relatively low resistivity. The large values of S show that the samples are semiconductors in the measured temperature range, inconsistent with the metallic T-dependence of ρ above 200 K. Positive values of S indicate the hole conduction. The S–T curves showed a jump at 280, 210 and 200 K with lowering temperature for the samples of $x=0$, 0.05 and 0.12, respectively. Small hysteresis was observed at each anomaly temperature. For the samples of $x=0.05$ and 0.12, the jump in the S–T curves seems to correspond to the minimum of ρ. Latent heat was not detected in DSC measurements at the transition temperature, in spite of the hysteresis in the S–T curves around the transition temperature.

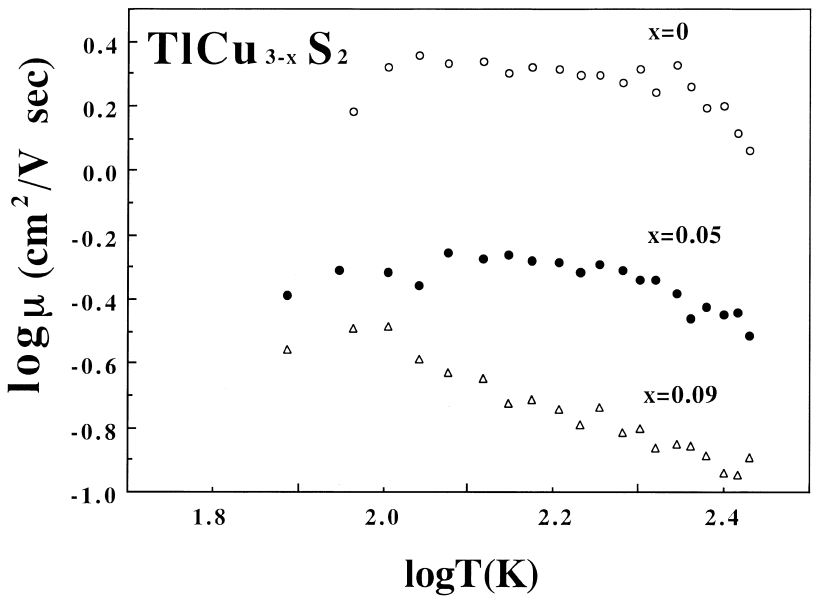

Fig. 5. Temperature variations of Hall mobility μ of $TlCu_{3-x}S_2$ ($x=0$, 0.05 and 0.09).

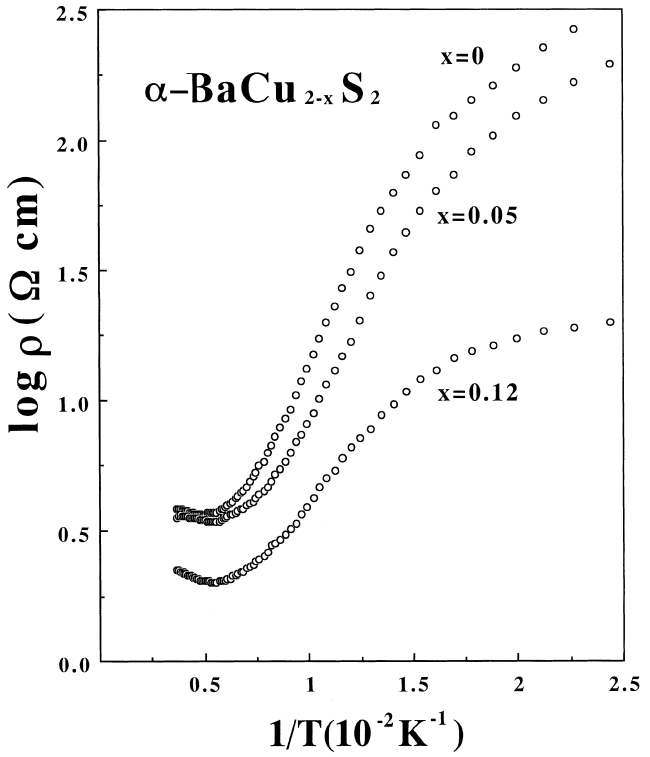

Fig. 6. Electrical resistivity ρ of α-$BaCu_{2-x}S_2$ ($x=0$, 0.05 and 0.12) as a function of temperature.

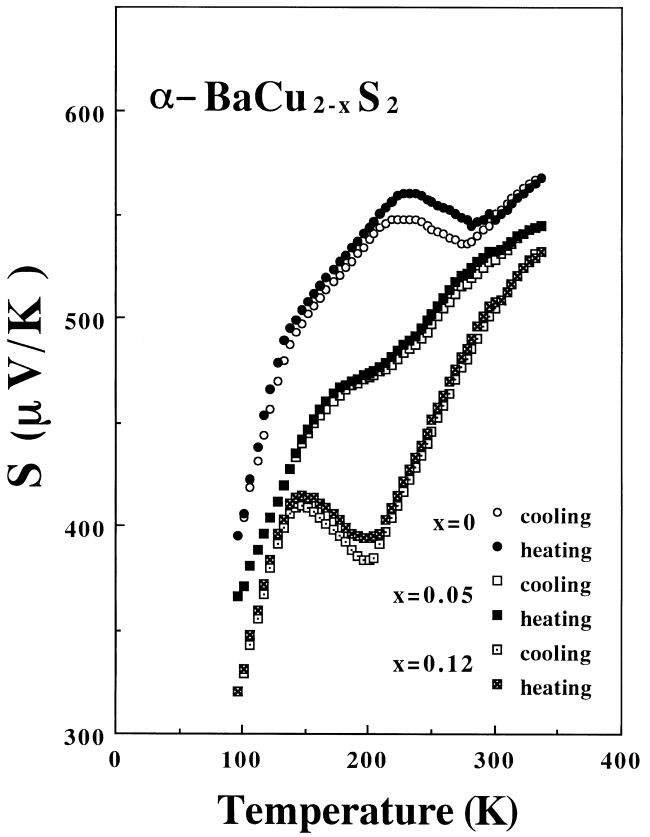

Fig. 7. Temperature dependences of Seebeck coefficients S for α-$BaCu_{2-x}S_2$ ($x=0$, 0.05 and 0.12).

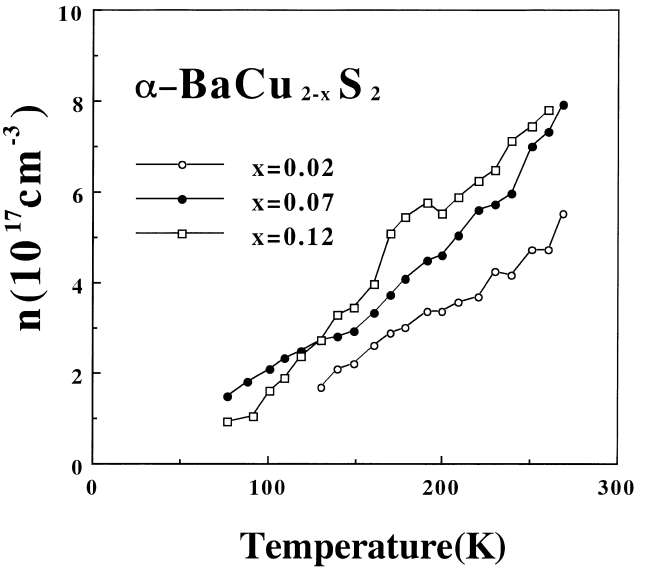

Fig. 8. Temperature variations of hole concentration n for α-$BaCu_{2-x}S_2$ ($x=0.02$, 0.07 and 0.12). Solid lines are guides to the eye.

Hall measurements showed that the conduction carriers are holes in all α phase samples. Fig. 8 gives temperature variations of hole concentration n for α-$BaCu_{2-x}S_2$ ($x=$ 0.02, 0.07, and 0.12). The values of n varied almost linearly with temperature for all samples. The observed values of n for all samples are fairly small compared with those calculated on the basis of the assumption that copper vacancies produce just the same number of holes; the calculated values of n were 2.03×10^{20}, 7.12×10^{20} and 12.2×10^{20} cm^{-3} for $x=0.02$, 0.07 and 0.12, respectively. These results may indicate that most of positive charges, which originate from copper vacancies, are not provided for the conduction carriers, but are localized at specific

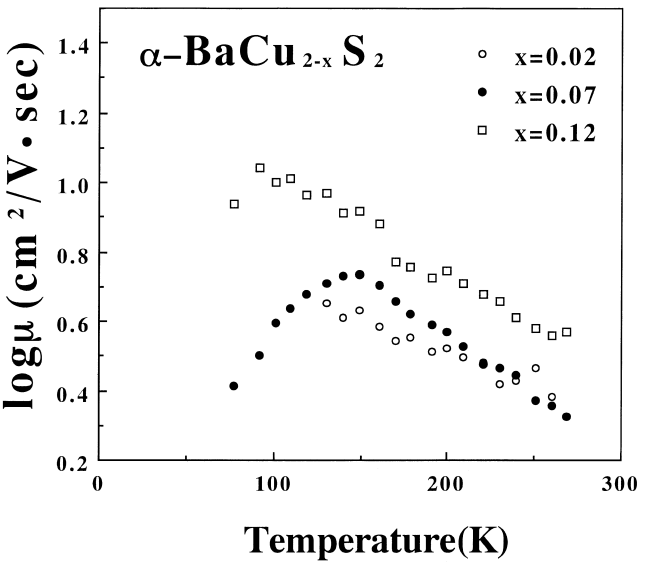

Fig. 9. Temperature variations of Hall mobility μ for α-$BaCu_{2-x}S_2$ ($x=0.02$, 0.07 and 0.12).

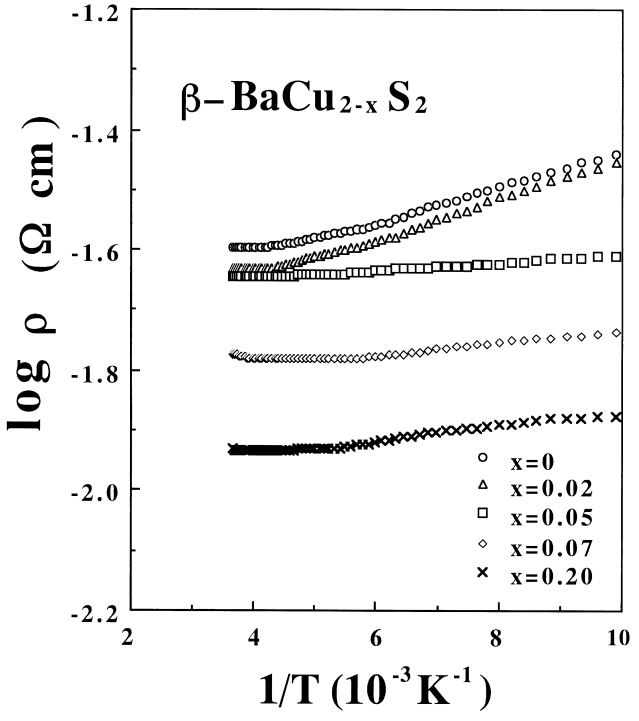

Fig. 10. Electrical resistivity ρ of β-$BaCu_{2-x}S_2$ ($x=0$, 0.02, 0.05, 0.07 and 0.20) as a function of temperature.

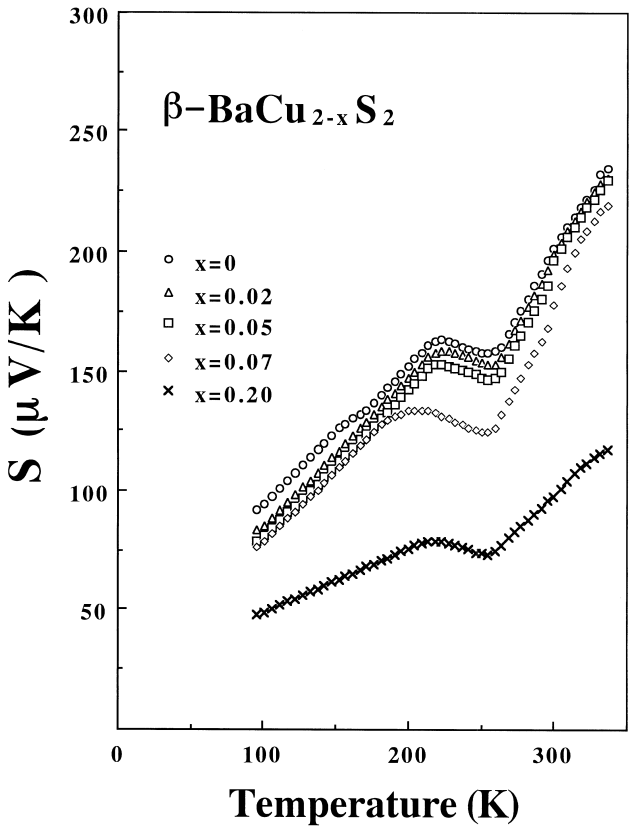

Fig. 11. Temperature variations of Seebeck coefficients S of β-$BaCu_{2-x}S_2$ ($x=0$, 0.02, 0.05, 0.07 and 0.20).

atomic sites: possibly at the sulfur sites. Fig. 9 shows temperature variations of Hall mobility μ for α-$BaCu_{2-x}S_2$ ($x=0.02$, 0.07 and 0.12). The Hall mobility for each sample showed a near $T^{-0.65}$ dependence above 150 K, implying that both acoustic phonon scattering and piezoelectric scattering are dominant scattering factors in the present conduction process. On the basis of the Seebeck and the Hall measurements, it could be concluded that α-$BaCu_{2-x}S_2$ is a semiconductor in the measured temperature range, in spite of the metallic temperature dependence of ρ above 200 K. The semiconductive nature is compatible with that the closed shell oxidation states of copper and sulfur in this compound.

3.4. Electrical properties of β-$BaCu_{2-x}S_2$

Temperature variations of ρ of β-$BaCu_{2-x}S_2$ ($x=0$, 0.02, 0.05, 0.07 and 0.20) are shown in Fig. 10. All samples showed a semiconductive behavior, exhibiting a small gradient change in the ρ–T curves at 200–250 K. The values of energy gap below 100 K were observed to be 0.0054, 0.0052, 0.0016, 0.0023 and 0.0017 eV, respectively for $x=0$, 0.02, 0.05, 0.07 and 0.20. The decreasing tendency of both the values of ρ and the energy gap with increasing x may imply that carriers are produced by the copper vacancies. Fig. 11 gives temperature variations of S for β-$BaCu_{2-x}S_2$ ($x=0$, 0.02, 0.05, 0.07 and 0.20). Positive values of S indicate the hole conduction. The values of S are rather high as compared with the low values of ρ. It is noted that the S–T curve in each sample showed a jump at 250 K with lowering temperature, and the gradient of the curves changed at ~250 K. These anomalies as well as small kinks in the ρ–T curves would show the existence of a phase transition at ~250 K. DSC measurements for these samples showed no latent heat from 110 to 273 K. We performed Hall measurements for β-$BaCu_{1.98}S_2$. The observed hole density n for this sample was 3.0×10^{20} cm^{-3} at 273 K and 2.5×10^{20} cm^{-3} at 77 K. These values of n are fairly identical with the calculated value of $n=2.1\times10^{20}$ cm^{-3}, which was obtained by assuming that the copper vacancies produce just the same number of holes.

4. Conclusions

$TlCu_{3-x}S_2$ was found to be stable in the composition range of $x\leqq0.05$. $TlCu_3S_2$ showed an incongruent melting at 680–692 K. $TlCu_{3-x}S_2$ exhibited a phase transition at ~100 K, which is characterized by a jump of resistivity (ρ) and a steep increase of Hall coefficient (R_H). It was found in the measurements of Seebeck coefficients (S) and Hall coefficients that the dominant carriers are holes, which are mainly produced from copper vacancies. The Hall mobility

scarcely changed at the transition temperature, suggesting that the transition has an electronic origin such as electron correlation effect.

α-$BaCu_2S_2$ was found to be stable below 800 K and β-$BaCu_2S_2$ above 800 K. The single phase region was $0 \leqq x \leqq 0.12$ for the α phase, and $0 \leqq x \leqq 0.20$ for the β phase. The α-$BaCu_{2-x}S_2$ was found to be a semiconductor with hole conduction in the measurements of ρ, S, and R_H. The values of S of the α phase are larger than 300 μV/K in the measured temperature region from 100 to 273 K. The $\rho-T$ curves of the α phase showed a minimum at ~200 K, suggesting a phase transition. The $S-T$ curves showed a jump at the transition temperature on cooling. The β-$BaCu_{2-x}S_2$ was found to be a semiconductor down to 2 K. The dominant carriers were observed to be holes in the measurements of S and R_H. The $\rho-T$ and the $S-T$ curves showed a phase transition at ~250 K. Hall measurements revealed that the copper vacancies are responsible for the hole conduction. The origins of the phase transitions observed in both α- and β-$BaCu_{2-x}S_2$ are not yet clear. Structural studies at low temperatures are needed.

Acknowledgements

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