

The crystal structure and electric conductivity of new quaternary chalcogenide halide CuHgSI

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Abstract

A novel compound CuHgSI was synthesized by solid-state reaction of CuI and HgS. The space group of the low-temperature phase has been determined to be $Pna2_1$ (No. 33) by the Rietveld refinement using the powder X-ray diffraction pattern. The electric conductivity at 491 K measured by the AC impedance method was $1.1 \times 10^{-5} \text{ S cm}^{-1}$. The ionic transport number measurements indicated that the Cu^+ ions constitute the majority charge carriers in these samples. The electronic contribution to the conduction process is small in comparison with the Cu^+ ionic contribution.

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1. Introduction

It is well known that copper and silver halides are cationic conductors. Many double salts of these halides with other compounds show higher conductivities at room temperature. For example, $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_3$ synthesized from CuCl, CuI and RbCl is the most well-known copper ion conductor [1].

Recently, a family of $M\text{HgSX}$ ($M = \text{Cu, Ag}$; $X = \text{Cl, Br, I}$) was prepared by combining copper or silver halides with HgS. The crystal structures of this material group have been examined by several authors: Guillo et al. [2] and Beck et al. [3] independently determined the crystal structures of CuHgSCl and CuHgSBr at room temperature, which were different from each other. Beck et al. also reported the crystal structures of CuHgSeBr, AgHgSBr, and AgHgSI [4]. AgHgSCl was synthesized and examined by Blachnik et al. [5]. They reported on the phase diagram of the AgCl–HgS system and lattice parameters of the constituent substances.

In this work, we investigated the synthesis, crystal structure, and electric conductivity of a new compound: CuHgSI. The crystal structure was determined by a Rietveld analysis of powder X-ray diffraction pattern. The electric conductivity was measured by an AC

impedance method, whereas the major charge carrier was determined by use of transport number measurements.

2. Experimental

CuHgSI was prepared by heating a stoichiometric mixture of CuI (Kojundo Chemical Lab. Co., purity 99.9%) and red-HgS (Kojundo Chemical Lab. Co., purity 99.9%) in an evacuated Pyrex tube at ca. 553 K for 2 weeks.

Differential thermal analysis (DTA) measurements were carried out between 100 and 650 K by use of a homemade apparatus.

Powder X-ray diffraction patterns were measured on a Rigaku RINT-2000 system using $\text{CuK}\alpha$ radiation at a scan rate of $0.5^\circ/\text{min}$ and a scan step of 0.02° .

The crystal structure of CuHgSI was initially estimated by the program EXPO [6], and successively refined by the Rietveld method using RIETAN-2000 program [7].

The electric conductivity was determined by an AC impedance method. The complex impedance measurements were performed by the two-terminal method using a computer-interfaced HIOKI 3532 LCR meter (42 Hz–5 MHz) in the temperature range from 300 to

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491 K. The pellet sizes were 13 mm in diameter and 1.0–1.4 mm thick. Carbon paints were applied on both sides of the pellet and electrodes to insure good electric contact with each other. The temperature of the sample was controlled within ± 1 K using a Chino KP1000 temperature controller equipped with Cu-Constantan thermocouples.

The ionic transport measurements were carried out using an “ion blocking” method and a non-“ion blocking” method. (i) In the non-“ion blocking” method, two pellets of the sample were sandwiched between copper electrodes. A constant DC current of 0.01 mA was applied across the sample for 3 days at 400 K using an ADVANTEST programmable DC voltage/current generator (TR6142). (ii) In the “ion blocking” method, two pellets of the sample were sandwiched between copper electrodes with carbon paints on both sides of the pellets. A constant DC voltage of 10 V was applied across the sample for 1–2 days at room temperature using ADVANTEST generator (TR6142). This method generates a polarization effect in the sample. The ionic transport number (t_{ion}) of the sample was estimated using the relation $t_{\text{ion}} = I_{\text{ion}}/I_{\text{tot}}$, where I_{ion} is the current due to the mobile ions and I_{tot} is the total current due to all charge carriers.

3. Results and discussion

3.1. DTA

The observed DTA curves of CuHgSI are illustrated in Fig. 1. An endothermic peak appeared at 611 K on heating but no exothermic peak was found on cooling in the first run. No thermal anomaly was found on heating and cooling processes in the second run. After annealing the sample at 473 K for 1 week, the thermal anomaly appeared again. Further experiments are in progress to assign this thermal anomaly.

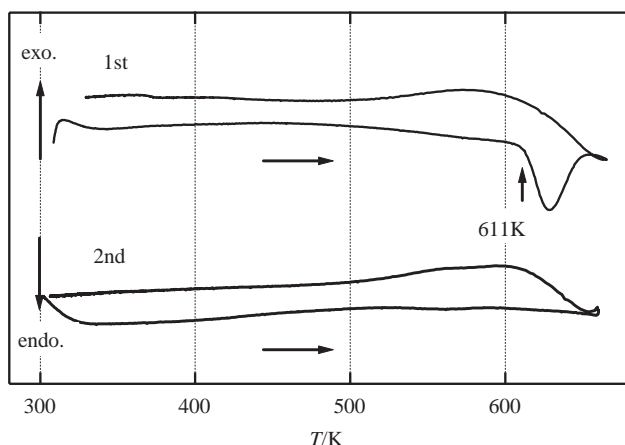


Fig. 1. DTA curves of CuHgSI.

CuHgSI was stable toward air and moisture at room temperature.

3.2. Powder X-ray diffraction pattern (XRD)

Fig. 2 shows the XRD patterns of CuHgSI measured at room temperature. The XRD pattern after heating up to 673 K (Fig. 2b) was completely different from the pattern before the heat treatment (Fig. 2a).

3.3. Crystal structures

The XRD pattern of the CuHgSI could be indexed in the orthorhombic system, $Pna2_1$. Fig. 3 shows the result of the Rietveld analysis of CuHgSI. The z position of Hg atom was fixed during the analysis due to freely floating origin along c . The experimental conditions and crystallographic data are summarized in Table 1. Table 2 shows the atomic positions and isotropic thermal parameters. Table 3 lists selected the interatomic distances and bond angles.

Fig. 4 illustrates the crystal structure of CuHgSI. All atoms occupy their sites completely. Cu–I and Hg–S bonds form zig-zag chains along the crystallographic c -axis. These chains arrange alternatively along the a - and

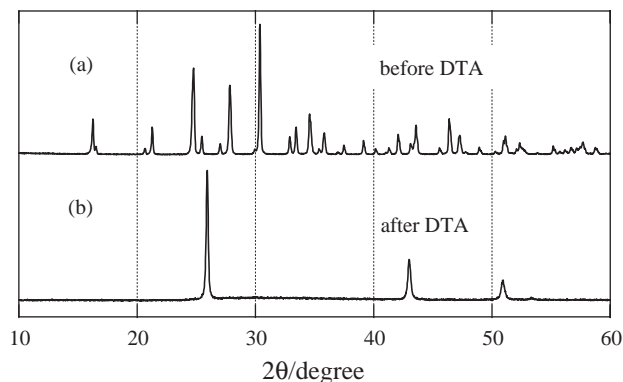


Fig. 2. Powder XRD patterns of CuHgSI at room temperature.

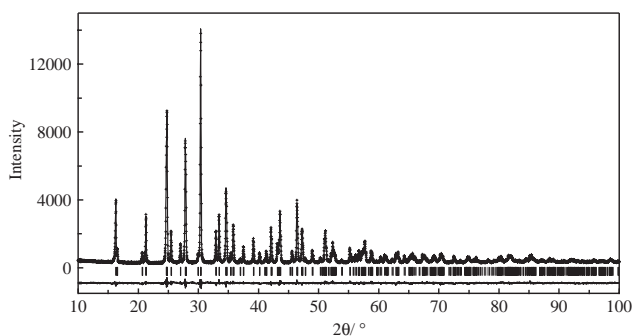


Fig. 3. Rietveld analysis of powder XRD pattern for CuHgSI at room temperature.

Table 1
Experimental conditions and crystallographic data of CuHgSI

Compound	CuHgSI
Space group	$Pna2_1$ (No. 33)
Crystal system	Orthorhombic
Lattice constants (Å)	$a = 7.1748(2)$ $b = 8.3356(2)$ $c = 6.9855(2)$
Volume (Å ³)	417.77(2)
Z	4
Range 2θ (°)	10–100
Scan step (°)	0.02
Structural parameters	15
Profile parameters	10 + 15*
Number of reflections	228
R_{wp} (%)	5.32
R_{exp} (%)	4.16
R_{Bragg} (%)	2.22

*Partial profile relaxation [7] $R_{wp} = \left[\frac{\sum_i \omega_i \{y_i - f_i(x)\}^2}{\sum_i \omega_i y_i^2} \right]^{1/2}$ $R_{exp} = \left[\frac{N - P}{\sum_i \omega_i y_i^2} \right]^{1/2}$ $R_{Bragg} = \frac{\sum_k |I_k(\text{obs}) - I_k(\text{cal})|}{\sum_k I_k(\text{obs})}$ y_i and $f_i(x)$ are the observed and calculated integrated intensities, respectively, and ω_i is the weight, N is the number of the data point, P is the number of the parameter, I_k is the Bragg intensity.

Table 2
Atomic positions and isotropic parameters of CuHgSI

Atom	x	y	z	U_{iso} (Å ²)
Cu	0.4189(5)	0.1336(4)	0.3874(5)	0.029(1)
Hg	0.0283(2)	0.0423(1)	0 (fixed)	0.031(1)
S	0.1095(9)	0.1548(6)	0.3008(9)	0.010(2)
I	0.4069(2)	0.1287(2)	0.7765(3)	0.016(1)

Table 3
Interatomic distances (Å) and bond angles (°) of CuHgSI.

Cu–S	2.324(2)	S–Cu–S	114.70(20)
Cu–I	2.649(3)	I–Cu–I	108.70(12)
Hg–S	2.373(5)	S–Hg–S	153.45(14)
Hg–I	3.213(2)	I–Hg–I	78.78(5)

b -axis. The Cu atoms are tetrahedrally coordinated by anions, where the Hg atoms are linearly coordinated by anions. This crystal structure can be compared with those of CuHgSCl and CuHgSBr [3]. In these materials, the forms of Hg–S chains are different from those of CuHgSI and the Hg atoms are surrounded by 4 halogens and 2 sulfur atoms. Further details of the crystal structure for CuHgSI can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49)7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD 413309.

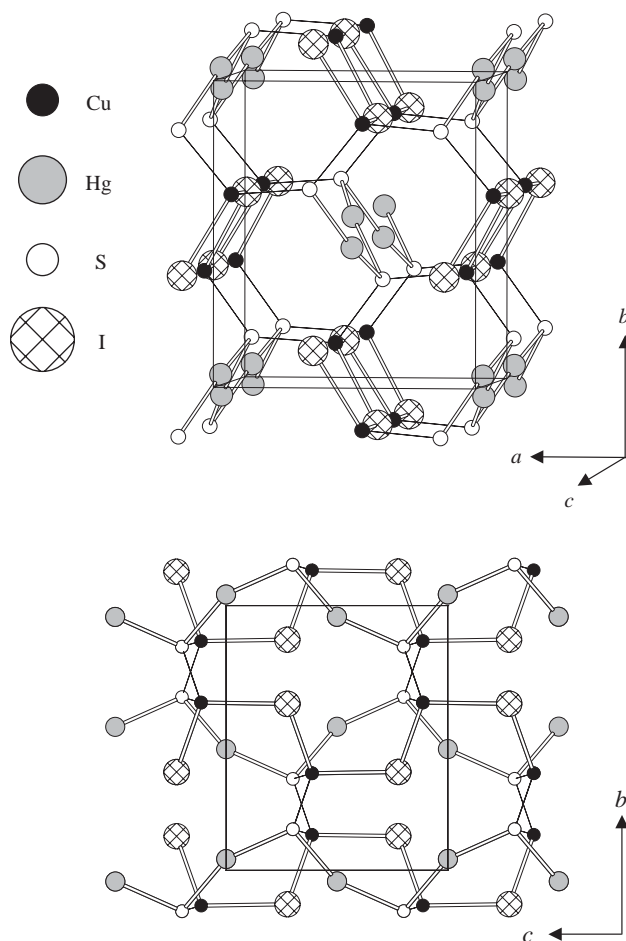


Fig. 4. Crystal structure of CuHgSI at room temperature.

3.4. Electric conductivity

3.4.1. AC impedance measurements

Fig. 5 shows the temperature dependence of electrical conductivities for CuHgSI. At the highest temperature (491 K), the electric conductivities increased up to $1.1 \times 10^{-5} \text{ S cm}^{-1}$. From the slope of the curve, the activation enthalpy, ΔH , for the conduction was determined to be 64 kJ mol^{-1} . Since all Cu sites are completely occupied, the ΔH value stands for the sum of formation enthalpy of defects and the activation energy of ionic motion [8].

3.4.2. Transport number measurements

Although ^{63}Cu NMR measurements resulted in a failure in monitoring the Cu ion dynamics probably due to the large quadrupole interaction, the transport number measurements by “ion blocking” and non-“ion blocking” methods indicate that the Cu ions constitute the major charge carriers in these phases.

In each measurement by the non-“ion blocking” method for both phases, a copper metallic luster was

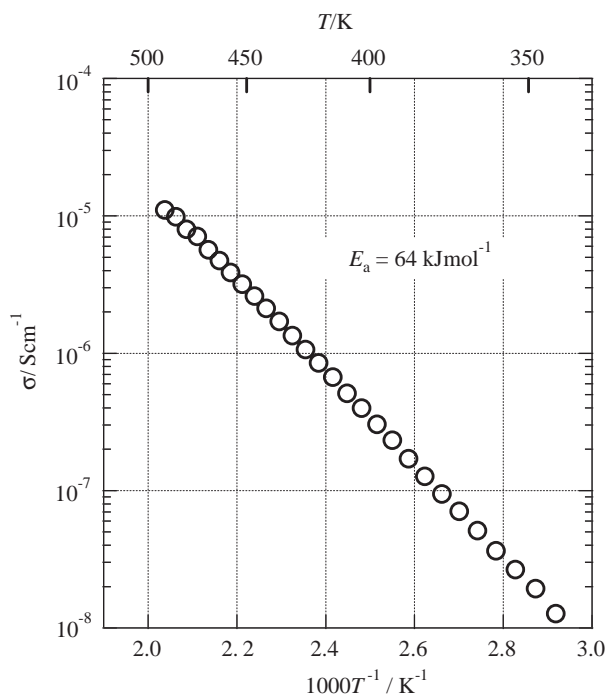


Fig. 5. Temperature dependence of electric conductivity in CuHgSI.

observed between the sample and the negative electrode. This fact clearly indicates that the Cu ions contribute to the electric conduction.

The value of ionic transport number determined by means of the “ion blocking” method reveals that the electronic fraction of the conduction process is about 20%.

4. Conclusion

A new compound CuHgSI was successfully synthesized and characterized. This substance has a novel crystal structure different from those of CuHgSCl and CuHgSBr. CuHgSI shows the Cu^+ ionic conductivity higher than those of CuHgSCl and CuHgSBr.

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