— Technical Paper —

Neutron Diffraction Study of CuClTe

Masaki HIROTA,^a Masaji ARAI,^a Takashi SAKUMA,^{a,*} and Yoshinobu ISHII^b^aDepartment of Physics, Faculty of Science, Ibaraki University (Mito 310-8512, Ibaraki)^bJapan Atomic Energy Research Institute (Tokai 319-1195, Ibaraki)

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The crystal structure of CuClTe has been analyzed by the Rietveld method with neutron powder diffraction data at 10 K, 290 K, 473 K and 633 K. The high temperature tetragonal phase including a statistical distribution of Cu atoms can be maintained in CuClTe even at 10 K. As the temperature increases, the inter atomic distances between Cu 4(b) and Cu 16(h) sites, Cu 16(h) and the first nearest Cu 16(h) sites, and Cu 16(h) and second nearest Cu 16(h) sites have a tendency to decrease. At high temperature Cu atoms would primarily diffuse through the route 4(b)→16(h)→4(a)→16(h)→4(b) sites along the *c*-axis.

Key Words : Solid Electrolytes, Neutron Diffraction, Crystal Structure, Electrical Conductivity

1 Introduction

A group of ternary copper halide-chalcogen compounds was synthesized about thirty years ago.¹⁾ The ionic conductivity of CuXTe (X=Cl, Br, I) was nearly two decades higher than that of corresponding copper halides in the temperature range 500-600 K.^{2, 3)} The low temperature phase transitions of CuXTe have been studied by specific heat measurements, electrical conductivity measurements and X-ray diffraction measurements.⁴⁻⁶⁾ New phase transitions in CuBrTe and CuITe were observed. The space group and the detailed atomic parameters (atomic positions, isotropic thermal parameters, occupation numbers for Cu sites) in CuITe at room temperature were determined.³⁾ However, the detailed crystal structure of CuClTe has not been reported.

The object of the present study is to determine the detailed crystal structure of CuClTe by the Rietveld method with neutron powder diffraction data in the temperature range 10-633 K. The temperature dependence of the crystal structure of CuClTe which would have a high temperature phase including a statistical distribution of Cu atoms is discussed.

2 Experimental

Stoichiometric quantities of copper chloride and tellurium were sealed in evacuated Pyrex tube, melted at 753 K for 3 hours, then annealed at 673 K for 1 day, 573 K for 3 days and 333 K for 1 day. The resulting compounds were crushed to a fine powder. Neutron diffraction measurements were collected from a powder CuClTe at 10, 290, 473 and 633 K with a triple-axis type spectrometer TAS-2 installed at JRR-3M in Japan Atomic Energy Research Institute. A vanadium container with 8 mm in diameter was used. The temperatures of cryostat (10 K, 290 K) and electric furnace (473 K, 633 K) could be stabilized to within ± 0.2 K. Neutron diffraction data were collected for 60 s per step at 0.1° intervals over the 2θ range of 5° to 100° by a step-scan mode. The incident

neutron wave length of $1.44 \text{ \AA}$ was used. The obtained diffraction patterns of CuClTe are shown in Fig. 1.

The powder sample for electrical conductivity was pressed at 700 kg/cm^2 into cylindrical pellets 1.3 cm in diameter and approximately 0.14 cm in length. Conductive silver paint was used to attach copper leads to a sample pellet while a Hioki 3531Z LCZ meter measured impedance throughout the frequency range 60 Hz-1 MHz. The conductivity of CuClTe was measured throughout the temperature interval 220 K-400 K and the resulting Arrhenius plot is shown in Fig. 2.

3 Results and Discussion

There are changes of the relative intensities in the neutron diffraction lines of CuClTe in the 2θ region of 40° to 50° in Fig. 1 by the change of the temperature. However, new reflections or super lattice lines did not appear at 10 K comparing with the reflections at 290, 473 and 633 K. Structural parameters of CuClTe were refined with RIETAN for Rietveld analysis.^{7, 8)} Structure refinements were performed by assuming that the space group of CuClTe is $I4_1/amd$. A unit cell which included 16 Cu atoms, 16 Cl atoms and 16 Te atoms was applied. There are 40 sites for 16 Cu atoms in the unit cell of CuClTe; two 4-fold sets designated 4(a), 4(b) and two 16-fold sets designated 16(b) and 16(h). Tables 1-4 show the final refined structural parameters of CuClTe. The present structural model having the disordered arrangement of Cu atoms can sufficiently explain the observed intensities. Atomic arrangements in CuClTe are shown in Fig.3. The pyroelectricity and the piezoelectricity for CuClTe are not expected to be observed. It is very rare that the high temperature phase including a statistical distribution of atoms can be maintained at 10 K. Typical copper halides (CuCl, CuBr, CuI)⁹⁾ and CuXTe (X=Br, I) undergo phase transitions from disordered arrangement of Cu atoms to ordered arrangements. In the case of ternary silver halide-chalcogen compounds (Ag_3SI , Ag_3SBr ,

Fig. 1 Rietveld refinement patterns for CuClTe. The broken lines are calculated intensities, the crosses (+) are observed intensities, and solid lines are the differences between calculated and observed intensities. The short vertical lines mark the positions of possible Bragg diffraction. (a) 10 K, (b) 290 K, (c) 473 K, (d) 633 K.

Fig. 2 Arrhenius plot of the electrical conductivity of CuClTe.

$\text{Ag}_3\text{SBr}_{0.5}\text{I}_{0.5}$) also undergo clear phase transitions from disordered arrangement of Ag atoms to ordered arrangements.⁹⁾

The occupation numbers for Cu sites in Tables 1-4 change rapidly by the change of temperature from 473 K

to 633 K; the occupation numbers for 4(b) and 16(g) sites decrease and those for 4(a) and 16(h) sites increase. The values of temperature parameters B for Cu, Cl and Te atoms increase as the temperature increases. The obtained values of temperature parameters for Cu atoms from Rietveld analysis are very large even at 10 K. However this would not show that the atomic vibrations of Cu atoms are very large at 10 K. The present structure model includes only 4(a), 4(b), 16(g) and 16(h) Cu sites. In practice a part of Cu atoms would be distributed on the other atomic positions leaving these Cu sites. The effect of the distribution of Cu atoms on other atomic positions would be included in the values of temperature parameters of Cu atoms at all temperatures. The probable atomic sites for Cu atoms are 8(e), 8(e), 16(h) and 32(i) Cu sites. 4(a), 4(b) and 16(g) sites are special positions of 8(e), 8(e) and 32(i) sites, respectively. In our recent

Fig. 3 Atomic arrangements in CuClTe. (a) 10 K, (b) 633 K.

test for the structural analysis of α -CuBrTe, the values of reliability factors with a disordered model including 8(e), 8(e), 16(h) and 32(i) Cu sites are less than those including 4(a), 4(b), 16(g) and 16(h) Cu sites. The values of lattice constant a show clear temperature dependence which is in contrast to a small change of lattice constant c in Tables 1-4.

Temperature change of values of Te-Cu 16(g) and Te-Te bond lengths in CuClTe is small. The calculated val-

Table 1 Structural parameters of CuClTe at 10 K. The coordinates x , y , z , isotropic thermal parameter B , lattice constants a , c and reliability factors R_{wp} , R_p , R_e , R_i , R_F .

Atom	Position	Occupation	x	y	z	$B (\text{\AA}^2)$
Cu	4a	0.03	0.0	0.75	0.125	2.74
	4b	0.77	0.0	0.25	0.375	3.22
	16g	0.72	0.127	0.377	0.875	1.72
	16h	0.08	0.0	0.168	0.651	1.68
Cl	16h	1.0	0.0	0.119	0.126	0.15
Te	16f	1.0	0.137	0.0	0.0	0.30

$$a = 15.537 \text{ \AA}, c = 4.799 \text{ \AA},$$

$$R_{wp} = 5.1\%, R_p = 4.0\%, R_e = 3.5\%, R_i = 2.6\%, R_F = 1.6\%$$

Table 2 Structural parameters of CuClTe at 290 K. The coordinates x , y , z , isotropic thermal parameter B , lattice constants a , c and reliability factors R_{wp} , R_p , R_e , R_i , R_F .

Atom	Position	Occupation	x	y	z	$B (\text{\AA}^2)$
Cu	4a	0.5	0.0	0.75	0.125	3.21
	4b	0.79	0.0	0.25	0.375	4.68
	16g	0.71	0.126	0.376	0.875	3.26
	16h	0.08	0.0	0.169	0.69	3.25
Cl	16h	1.0	0.0	0.118	0.128	1.23
Te	16f	1.0	0.137	0.0	0.0	0.72

$$a = 15.637 \text{ \AA}, c = 4.818 \text{ \AA},$$

$$R_{wp} = 5.4\%, R_p = 4.2\%, R_e = 4.3\%, R_i = 3.9\%, R_F = 2.4\%$$

Table 3 Structural parameters of CuClTe at 473 K. The coordinates x , y , z , isotropic thermal parameter B , lattice constants a , c and reliability factors R_{wp} , R_p , R_e , R_i , R_F .

Atom	Position	Occupation	x	y	z	$B (\text{\AA}^2)$
Cu	4a	0.07	0.0	0.75	0.125	5.60
	4b	0.57	0.0	0.25	0.375	5.17
	16g	0.70	0.125	0.375	0.875	5.30
	16h	0.14	0.0	0.197	0.625	5.25
Cl	16h	1.0	0.0	0.119	0.125	2.86
Te	16f	1.0	0.14	0.0	0.0	2.11

$$a = 15.703 \text{ \AA}, c = 4.803 \text{ \AA},$$

$$R_{wp} = 4.8\%, R_p = 3.8\%, R_e = 4.2\%, R_i = 6.1\%, R_F = 3.8\%$$

Table 4 Structural parameters of CuClTe at 633 K. The coordinates x , y , z , isotropic thermal parameter B , lattice constants a , c and reliability factors R_{wp} , R_p , R_e , R_i , R_F .

Atom	Position	Occupation	x	y	z	$B (\text{\AA}^2)$
Cu	4a	0.13	0.0	0.75	0.125	5.49
	4b	0.46	0.0	0.25	0.375	5.37
	16g	0.65	0.128	0.378	0.875	5.81
	16h	0.20	0.0	0.19	0.628	5.97
Cl	16h	1.0	0.0	0.119	0.124	4.39
Te	16f	1.0	0.139	0.0	0.0	3.54

$$a = 15.869 \text{ \AA}, c = 4.789 \text{ \AA},$$

$$R_{wp} = 4.0\%, R_p = 3.1\%, R_e = 3.6\%, R_i = 6.3\%, R_F = 4.9\%$$

ues of Te-Cu 16(g) and Te-Te bond lengths in CuClTe at 10 K are 2.63 and 2.75 $\text{\AA}$, respectively. The values at 633 K are 2.64 and 2.77 $\text{\AA}$. It is possible that the atomic types of the neighbors of the tellurium atoms are tellurium atoms in copper halide-chalcogen compounds. The tellurium atoms in CuClTe form infinite helical chains that are known in metallic tellurium. The Cl atoms keep off other Cl atoms, and the nearest neighbors of Cl atoms are Cu atoms because of attractive forces between them. The nature of a bond between Cu and Cl atoms may be ionic, and that between tellurium atoms covalent. In the case of Ag_3SI , which is a well known ternary silver halide-chalcogen compound, the formal charges of Ag, S and I are +1, -2 and -1, respectively.¹⁰⁾ The sulphur atoms keep off other sulphur atoms in the silver halide-chalcogen compounds. On the contrary, it is possible that the atomic types of the nearest neighbors of the tellurium atoms are tellurium atoms in copper halide-chalcogen compounds.

The calculated inter atomic distances from the atomic positions, which show apparent temperature dependence, are given in Table 5. The inter atomic distances between Cu 4(b) and Cu 16(h) sites (r), Cu 16(h) and the first nearest Cu 16(h) sites (r_1), and Cu 16(h) and second nearest Cu 16(h) sites (r_2) have a tendency to decrease. The values of r_1 and r_2 are sides of tetrahedron which surrounds Cu 4(b) site in Fig.3. This shows that the volume of tetrahedron formed by four Cu 16(h) sites decreases although the volume of unit cell increases with temperature. At 10 K the volume of tetrahedron which surrounds 4(b) site (2.874 $\text{\AA}^3$) is greater than that of the tetrahedron for 4(a) site (2.332 $\text{\AA}^3$). The volume of tetrahedron for 4(b) site (1.464 $\text{\AA}^3$) is almost same as that of 4(a) site (1.430 $\text{\AA}^3$) at 633 K.

From the conductivity measurement of CuClTe throughout the temperature interval 220 K - 400 K, an anomaly of electrical conductivity was not observed in Fig.2. The obtained value of the electrical conductivity at room temperature coincides with that of the former reports above room temperature.²⁾ An estimate of the activation energy E can be made by fitting acquired data for CuClTe to the expression $\sigma T = A_0 \exp(-E/kT)$. The value of 0.42 eV for the activation energy of CuClTe was estimated. The solid lines in Fig.2 associated with the CuClTe are a least-square fit of the data. 4(a), 4(b), 16(h) Cu sites are surrounded with a tetrahedron which is constructed from four Cl atoms. Cu atoms would diffuse from a Cu site in one tetrahedron to other Cu site in the nearest tetrahedron through a triangular surface which is

Table 5 Temperature dependence of inter atomic distances between Cu 4(b)-Cu 16(h) sites (r), Cu 16(h)-first nearest Cu 16(h) sites (r_1) and Cu 16(h)-second nearest Cu 16(h) sites (r_2).

	$r(\text{\AA})$ Cu 4(b)-Cu 16(h)	$r_1(\text{\AA})$ Cu 16(h)-Cu 16(h)	$r_2(\text{\AA})$ Cu 16(h)-Cu 16(h)
10 K	1.84	2.56	3.21
290 K	1.98	2.53	3.53
473 K	1.46	1.67	2.67
633 K	1.52	1.91	2.78

decided by three Cl atoms. There is not very much change in the triangular surface with temperature. The estimated value of the activated energy from Fig. 2 was 0.42 eV throughout the temperature interval 200 K–400 K. It would suggest that the value of the activation energy is mainly affected by the triangular surface decided by Cl atoms. The change of the activation energy has not been observed in the α -phase of copper halidechalcogen solid electrolytes. In the case of CuTe⁶⁾, the activation energy was 0.57 eV throughout the α - and β -phases. To estimate the change of activation energy in CuClTe in detail, we need a measurement of the electrical conductivity over a wide temperature range. The electric conductivity would be related to a statistical occupation of Cu atoms. Cu atoms would diffuse in CuClTe through the disordered Cu sites. As the temperature increases, the distance between 4(b) and 16(h) sites decreases from 1.9 to 1.5 Å in Table 5. The increase of the electrical conductivity would be related to the decrease in the distance between 4(b) and 16(h) sites. From the distances between neighboring atoms at high temperature Cu atoms would primarily diffuse through the route 4(b)→16(h)→4(a)→16(h)→4(b) sites along the c -axis. As the crystal struc-

ture of CuClTe belongs to tetragonal system, the electrical conductivity would show anisotropic properties. To study further details of the dynamical behavior of CuClTe, the single crystal is required.

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