

## PHASE TRANSITION OF CuITe

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### Abstract

The phase transition and the crystal structures of CuITe were investigated by differential thermal analysis and X-ray powder diffraction measurements in the temperature range between 300 and 683 K. The new phase transition in CuITe was observed at 592 K. The enthalpy of transition is  $\Delta H=0.125 \text{ kJ mol}^{-1}$ . The new phase above 592 K belongs to tetragonal system with the space group  $I4_1/amd$ .

**Keywords:** CuITe, DSC, solid electrolytes, X-ray diffraction

### Introduction

CuITe is one of the copper halide–chalcogen compounds which have high ionic conductivity and the diversity of crystalline structures. An early investigation [1] of the compound reported the ionic conductivity of about  $10^{-5} \text{ S cm}^{-1}$  at room temperature compared with a small electronic contribution (less than  $10^{-8} \text{ S cm}^{-1}$ ) and also confirmed the existence of a second-order phase transition at 281 K. Several X-ray diffraction studies [2, 3] in the temperature range between 10 and 473 K provided convincing evidence of a structural phase transition with distinct lattice changes. The high temperature phase above 281 K belonged to the tetragonal system with the space group  $I4_1/amd$  and the copper atoms were in disordered arrangement. The low temperature phase belonged to the orthorhombic system. Calorimetric measurement [4] in the temperature range between 100 and 473 K showed that the specific heat anomaly due to the transition at 281 K is relatively small. However, recent ionic conductivity measurement [5] could not detect any anomalous electrical behavior at 281 K.

Although some studies have been made on the properties of CuITe below 473 K as described above, any studies have not been reported above 473 K. In the present study, specific heat and X-ray diffraction measurements have been carried out above 473 K, and a new phase transition was found at 592 K. The enthalpy of transition was calculated, and the space group of the higher temperature phase was also determined.

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## Experimental

CuTe was initially prepared from CuI (99.5%) and Te (99.99%). Stoichiometric quantities of CuI and Te were weighted and enclosed in a pyrex tube in vacuum and melted at 753 K for three hours. After solidification it was annealed at 673 K for 1 day, 573 K for 3 days and 333 K for 1 day. The resulting compound was crushed to a fine powder. Heat-flux differential scanning calorimetry (DSC) measurement was performed from 300 to 683 K at a scanning rate of 10 K min<sup>-1</sup> using a Shimadzu DSC-50 thermal analyzer. The measurement was made in a flowing N<sub>2</sub> atmosphere. The powder sample of 25.67 mg was encapsulated in aluminium pan.

The X-ray diffraction pattern of CuTe was measured with the powder sample at 300 and 620 K. X-ray diffraction data were collected using CuK<sub>α</sub> radiation monochromatized with PG 002 reflection for 5 s per step at 0.05° intervals over the 2θ range of 10 to 90° by a step-scan mode.

## Results and discussion

The melting point of CuTe is 715 K, but CuTe begins to separate into CuI and CuTe<sub>2</sub> above 650 K. Figure 1 shows the DSC traces for CuTe in the temperature range between 550 and 620 K. A new specific heat anomaly was observed. An endothermic peak  $T_{c1}$  is observed at 592 K on heating and an exothermic peak  $T_{c2}$  is observed at 587 K on cooling, respectively. Since the latent heat is not observed, it might be second-order phase transition. The enthalpy of new phase transition was estimated to be 0.125 kJ mol<sup>-1</sup> from a computation of the peak area. The transition temperature  $T_c$ , enthalpy  $\Delta H$  of typical copper halide [6, 7] and copper halide–chalcogen [4] compounds are listed in Table 1.

The enthalpy of transition at 592 K in CuTe is same order as that at 281 K in Table 1. This table shows that enthalpy of copper halide–chalcogen compounds is smaller compared with that of copper halide compounds. Copper distribution of copper halide–chalcogen compounds changes with phase transition. However the atomic arrange-

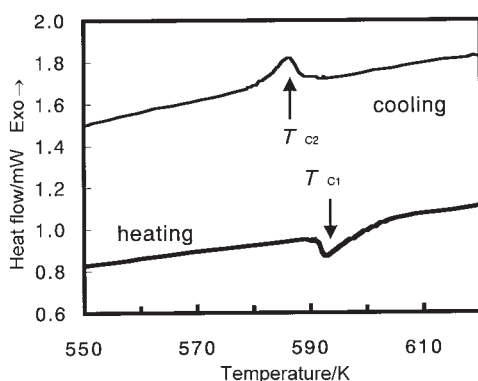


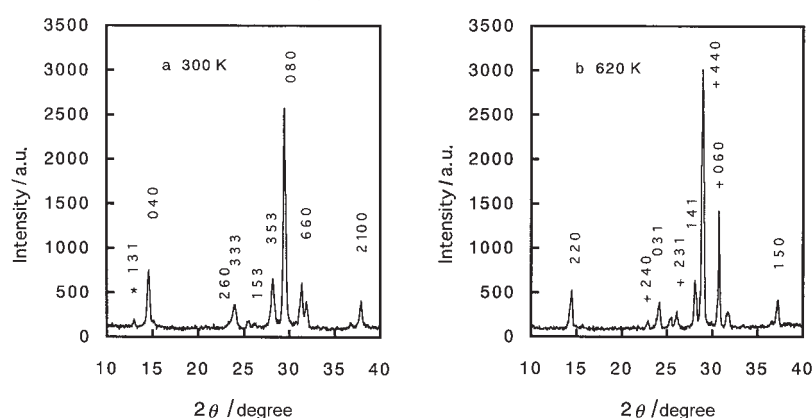
Fig. 1 Differential scanning calorimetry (DSC) heating and cooling traces for CuTe

ment of halogen or chalcogen, which form the framework of a lattice, hardly changes. It might be considered that the anomaly is mainly from the change of copper distribution.

**Table 1** The transition temperature ( $T_c$ ) and enthalpy ( $\Delta H$ ) of copper conduction solids

Compound	$T_c$ /K	$\Delta H$ /kJ mol <sup>-1</sup>
CuI	642	7.113
	680	3.222
CuBr	658	5.858
	743	2.929
CuTe	281	0.281
	592	0.125
CuBrTe	230	0.048
	351	0.478
CuTe <sub>2</sub>	286	0.056

We could conclude that the new phase transition exists at 592 K in CuTe. This idea is supported by the result of X-ray diffraction measurements. The observed X-ray diffraction patterns over the  $2\theta$  range of 10 to 40° below and above the new transition temperature are shown in Figs 2a (300 K) and 2b (620 K). The intensity of reflections at 620 K which are indicated by mark + is stronger than that at 300 K through the phase transition. Further the weak reflection at 300 K which is indicated by the mark \* in Fig. 2a disappears at 620 K. The reflections at 620 K in Fig. 2b were thoroughly indexed with the tetragonal cell. Considering systematic absence of reflections, it is found that the high temperature phase above 592 K belongs to the tetragonal system with the space group  $I4_1/amd$  (No. 141) which was proposed for the crystal structure at room temperature by Alpen *et al.* [1]. When we apply the same unit cell to the reflections in X-ray pattern at 300 K, the mark \* at 300 K in Fig. 2a



**Fig. 2** X-ray diffraction patterns of CuTe at (a) 300 K and (b) 620 K. The reflections at 300 and 620 K were indexed with the orthorhombic cell ( $(\sqrt{2}a \times \sqrt{2}b \times 3c)$  ( $a \approx b$ )) and the tetragonal cell ( $a \times a \times c$ )

corresponds to the 150 reflection. The presence of 150 reflection does not correspond to the condition of the limiting possible reflections in the space group  $I4_1/amd$ . We need to reconsider the crystal structure between 281 and 592 K.

The new phase transition at 592 K separates the high temperature phase from the room temperature phase while the transition at 281 K separates the room temperature phase from the low temperature phase. We analyzed the crystal structure of high temperature phase in CuTe with Rietan [8, 9]. The lattice constants of the high temperature phase are  $a=17.44 \text{ \AA}$  and  $c=4.76 \text{ \AA}$  at 620 K. The high temperature phase belongs to the tetragonal system  $a \times a \times c$  with the space group  $I4_1/amd$ . 16 CuTe molecules are included in the unit cell. Iodine atoms and tellurium atoms exhibit ordered arrangement. We need 40 or 64 sites for 16 copper atoms in the unit cell to explain the diffraction profile. As there is almost no difference in  $R$  factor for the case of 40 sites and that for 64 sites at present, we could not definitely conclude the crystal model.

The existence of a similar high temperature phase transition at 592 K in CuTe has been recognized in CuBrTe [10]. CuBrTe exhibits the  $\alpha$ - $\beta$  phase transition at 351 K and  $\beta$ - $\gamma$  phase transition at 230 K.  $\alpha$ -CuBrTe and  $\beta$ -CuBrTe belong to the tetragonal system  $a \times a \times c$  and orthorhombic system  $\sqrt{2}a \times \sqrt{2}b \times 3c$  ( $a \approx b$ ), respectively. Super lattice lines that disappear in  $\alpha$ -CuBrTe appear in  $\beta$ -CuBrTe. The weak reflection indicated by the mark \* at 300 K in Fig. 2a appears in the room temperature phase in CuTe. The reflection would be related to a super lattice line. When we assume that the room temperature phase of CuTe belongs to the orthorhombic system  $\sqrt{2}a \times \sqrt{2}b \times 3c$  ( $a \approx b$ ), all of the indexes of the reflection lines could be given as in Fig. 2a. The detailed analysis for structural parameters (atomic positions, isotropic thermal parameters) is now in progress. Both the theoretical and experimental studies are further needed on the phase transitions and the diffusion mechanism in CuTe.

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