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Structural Phase Transitions of Polycrystalline Cu_4SeTe

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Abstract—Phase transitions of powder Cu_4SeTe have been studied by high-temperature X-ray diffraction in the temperature range 300–1125 K. The results demonstrate that the low-temperature, hexagonal phase α-Cu_4SeTe ($a = 4.1880$ Å, $c = 41.8531$ Å, $V = 636.71$ Å^3, sp. gr. $P6_1$, $Z = 6$, $\rho_{calc} = 7.2622$ g/cm^3) is a β-Cu_2Te-based superstructure. Above 700 ± 3 K, Cu_4SeTe transforms into a cubic (γ) phase ($a = 6.0672$ Å, $V = 223.339$ Å^3, sp. gr. $Pa\bar{3}$, $Z = 4$).

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INTRODUCTION

Thermomagnetic and thermoelectric materials with low lattice thermal conductivity and high carrier mobility have a wide application area as thermoelectric power converters [1–3]. They include superionic silver and copper chalcogenides and a variety of their solid solutions. Clearly, the ability to effectively employ such materials is highly dependent on the availability of experimental data on the effect of external factors on their structure and structural changes. Note that a characteristic feature of these chalcogenides is that they undergo polymorphic transformations on heating. In this paper, we report the synthesis and structural phase transitions of polycrystalline Cu_4SeTe.

EXPERIMENTAL

To prepare Cu_4SeTe samples for this investigation, elemental Cu, Se, and Te of 99.998+% purity were melted together in an evacuated ($\simeq 10^{-2}$ Pa) silica ampule in a tilted (20°) single-zone furnace. The ampule, 20 cm in length, containing 5 g of a starting mixture, was gradually introduced into the furnace, preheated to 1200 ± 5 K. After the entire ampule was introduced into the furnace, its temperature was raised to 1300 K and held there for 1.5 h. Next, the furnace temperature was lowered to 750 K, and the ampule and material were homogenized at this temperature for five days. After annealing, the resultant material had the form of a dark gray alloy ingot.

All experiments aimed at identifying structural phase transitions of Cu_4SeTe were carried out on a D8 Advance powder X-ray diffractometer (Bruker, Germany) in a vacuum of $\simeq 1.3$ Pa at temperatures from 300 to 1100 K (40 kV, 40 mA, CuK_α radiation, $\lambda = 1.5406$ Å, $10° \leq 2\theta \leq 70°$).

EXPERIMENTAL RESULTS

For the purpose of this study, fine powders were prepared from the Cu_4SeTe ingot and characterized by X-ray diffraction at temperatures from 300 to 1150 K, mainly at 100-K intervals. To accurately determine the temperature at which the diffraction pattern changed, X-ray diffraction patterns were also taken at 50-, 25-, 10-, and 5-K intervals. Note that the heating rate was 2 K/min. Before collecting each X-ray diffraction pattern, we held the sample at a fixed temperature for 20 min.

Clearly, to identify possible phase transitions of Cu_4SeTe, it was necessary, first of all, to determine the lattice parameters of its low-temperature phase. To this end, we obtained X-ray diffraction patterns of fine powders of the synthesized Cu_4SeTe sample under a vacuum of 0.8 Pa at a temperature of 300 K. The X-ray diffraction data obtained for the low-temperature phase were analyzed using TOPAS profile and structure analysis software. The results demonstrate that, at room temperature, the material under consideration has a hexagonal structure, which can be thought of as a β-Cu_3Te-based superstructure. The 300-K parameters of its hexagonal lattice, refined using EVA software, are $a = 4.1880$ Å, $c = 41.8531$ Å, and $V = 636.71$ Å^3 (sp. gr. $P6_1$, $Z = 6$, $\rho_{calc} = 7.2622$ g/cm^3). The X-ray diffraction data for the low-temperature phase are presented in Table 1, and its X-ray diffraction pattern is shown in the figure (scan *1*).

In our high-temperature studies of Cu_4SeTe in the range 300–1150 K, the temperature of the sample was controlled automatically. Significant changes were detected at temperatures of 573, 673, 723, and 773 K; that is, at temperatures from 300 to 573 K, the sample experiences no structural changes (figure, scans *1*–*3*).

It is seen in the figure that, at a temperature of 573 K (scan *4*), the intensity of the reflections at $2\theta = 12.714°$ and $2\theta = 25.959°$ changes markedly; new, rather strong reflections emerge at $2\theta = 25.587°$ and

Table 1. 300-K X-ray diffraction data for Cu_4SeTe (hexagonal structure, $a = 4.1880$ Å, $c = 41.8531$ Å)

2θ, deg	I, %	hkl	d_{obs}, Å	d_{calc}, Å	Δd, Å
12.651	41	0 0 6	6.97478	6.97588	−0.00110
24.595	2.7	1 0 2	3.61472	3.61325	0.00147
26.725	100	0 0 12	3.49217	3.48759	0.00458
28.716	14.7	1 0 5	3.33293	3.32792	0.00501
34.060	2.2	1 0 7	3.10615	3.10100	0.00515
37.273	3.2	1 0 11	2.62792	2.62535	0.00257
38.723	7	0 0 13	2.40996	2.40771	0.00195
43.113	2.1	0 0 18	2.32377	2.32511	0.00134
44.391	1.9	1 0 6	2.09663	2.09432	0.00231
50.732	27.9	1 1 0	2.03909	2.03704	0.00205
50.808	16.3	1 0 7	1.79810	1.79812	0.00002
51.461	6	1 1 6	1.79556	1.79501	0.00055
52.377	8	1 1 9	1.77432	1.77255	0.00177
63.521	2	1 0 19	1.74538	1.74401	0.00137
67.031	4	2 0 2	1.39501	1.39505	0.00004

Table 2. 800-K X-ray diffraction data for Cu_4SeTe (cubic structure, $a = 6.0672$ Å)

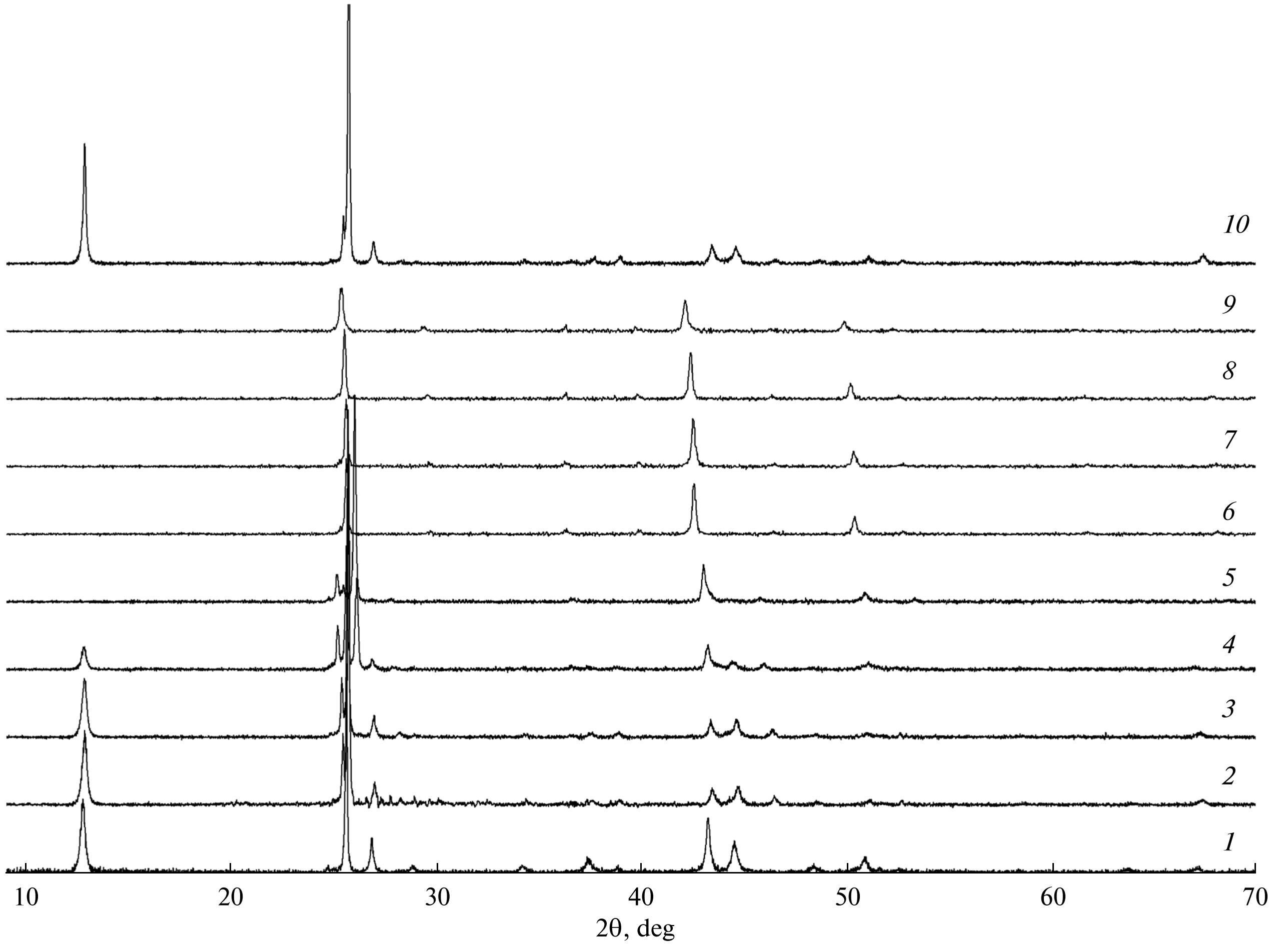
2θ, deg	I, %	hkl	d_{obs}, Å	d_{calc}, Å	Δd, Å
25.345	100	1 1 1	3.51130	3.50289	0.00841
29.331	15	2 0 0	3.04752	3.0336	0.01392
36.201	25	2 1 1	2.47939	2.47692	0.00247
42.058	85	2 2 0	2.14664	2.14508	0.00156
49.785	25	3 1 1	1.83005	1.82933	0.00072
52.239	8	2 2 2	1.74972	1.75145	0.00173
61.047	2	4 0 0	1.51666	1.51680	0.00014
67.281	3	3 3 1	1.39049	1.39191	0.00142

$2\theta = 26.750°$; and a number of weak reflections disappear. It is of interest to note that, in this process, the X-ray diffraction pattern of the low-temperature phase changes insignificantly. For this reason, the presence of two reflections with interplanar spacings $d = 3.5465$ and 3.4296 Å, among the more than 20 reflections from the low-temperature phase, cannot be thought of as evidence of a phase transition, but they indicate the onset of a transition. According to a calculational analysis of individual peaks, the reflection with $d = 3.5465$ Å, having the Miller indices 311, arises from an intermediate cubic phase with a unit-cell parameter $a \simeq 11.82$ Å, and the reflection with $d = 3.4296$ Å, having the Miller indices 111, is due to a cubic phase with a unit-cell parameter $a = 5.96$ Å at $T = 573$ K. As mentioned above, the next change in the X-ray diffraction pattern occurs near $T = 673$ K (figure, scan *5*). At 673 K, almost all the reflections from the low-temperature phase disappear, and the system becomes a mechanical mixture of two cubic phases with unit-cell parameters $a \simeq 6.05$ Å and $a \simeq 11.83$ Å (scan *6*). At 723 K (scan *6*), all of the reflections from the cubic superlattice disappear and we observe new reflections from a cubic sublattice and two peaks of medium intensity: 521 with $d = 2.2647$ Å and 600 with $d = 1.9589$ Å.

The changes observed above 773 K (scan *8*) are due to the completion of the phase transition, after which the material consists of a cubic phase with $a = 6.067$ Å and $V = 223.34$ Å^3 (sp. gr. $Pa\bar{3}$). The crystallographic data for this phase are presented in Table 2. Note that the phase transition is reversible, as evidenced by the fact that scan *10* in the figure is identical to scan *1*.

DISCUSSION

It is worth pointing out that phase formation processes in the Cu–X (X = S, Se, Te) systems are very complex and depend on many factors, such as the mixed valence state of the copper atoms (Cu^+ and



X-ray diffraction patterns of Cu_4SeTe after heating to (*1*) 300, (*2*) 373, (*3*) 473, (*4*) 573, (*5*) 673, (*6*) 723, (*7*) 773, (*8*) 873, and (*9*) 1150 K and (*10*) subsequent cooling to 300 K.

Cu^{2+}), their high mobility, and the presence of copper in linear, planar, or polyhedral coordination. These factors have a significant effect on the structure and physical properties of the materials and the possibility of obtaining single-phase samples. Because of this, results reported by different researchers do not always agree well [4–8]. For example, Stevels and Jellinek [8] investigated phase relations along the pseudobinary join Cu_2Se–Cu_2Te of the Cu–Se–Te system and identified a new, monoclinic phase with unit-cell parameters $a = 3.60$, $b = 4.166$, $c = 6.930$ Å, and $\beta = 95.18°$ ($Z = 1$). These parameters are inconsistent with data for Ag_4SeTe, Ag_4SSe, and Ag_2STe and with the present results. On the other hand, the lattice parameter of 3.60 Å appears unacceptable for a compound containing Se and Te, which have ionic radii of 1.93 and 2.11 Å, respectively. In our opinion, the diffraction data reported by Stevels and Jellinek [8] can be interpreted in terms of a hexagonal lattice and correspond to the structure of the phase β-Cu_2Te [9] with unit-cell parameters $a = 4.246$ Å and $c = 7.289$ Å.

Gasimova et al. [9] investigated phase transformations in polycrystalline samples of the $Cu_4Se_{1.5}Te_{0.5}$ solid solution. Their results demonstrate that the low-temperature phase of $Cu_4Se_{1.5}Te_{0.5}$ has a hexagonal structure with lattice parameters $a = 4.162$ Å and $c = 20.66$ Å (sp. gr. $R\bar{3}m$, $Z = 3$) and is a three-slab polytype with the β-Cu_2Te structure. At a temperature of ≃573 K, this phase transforms into a cubic phase with a unit-cell parameter $a = 5.84$ Å (sp. gr. $Fm\bar{3}m$, $Z = 4$); that is, it undergoes a direct phase transformation, without formation of an unstable intermediate phase. With increasing temperature, the amplitude of lattice vibrations of the copper atoms increases and, in the case of orientation coupling between phases, an energetically favorable condition for the formation of a cubic phase becomes fulfilled.

The cubic phase of Cu_4SeTe forms near 700 K, in contrast to $Cu_4Se_{1.5}Te_{0.5}$ ($T_{\text{transition}} = 800 \pm 5$ K), and has a different symmetry group ($Fm\bar{3}m$ and $P\bar{4}3m$, respectively). Thus, the Se : Te ratio directly influences the phase formation process in these systems. As a result, it may cause changes not only in the physicochemical properties and structure of the material but also in the mechanism of structural transformations. We assume that, in this case, at $T \simeq 473$ K the cubic phase of Cu_4SeTe nucleates at defects and slowly grows within the low-temperature phase. The phase transition reaches completion near 700 K. Such a mechanism of phase transformations is known to be inherent in many chalcogenides: ZnS, CdS, $Cu_2S(Se)$, Cu_3VS_4, $CuFeS_2$, and others.

CONCLUSIONS

The present results demonstrate that the Cu_2Se–Cu_2Te system contains a solid solution of composition Cu_4SeTe with a hexagonal structure and lattice parameters $a = 4.1880$ Å, $c = 41.8531$ Å, and $V = 636.71$ Å^3 (sp. gr. $P6_1$, $Z = 6$, $\rho_{calc} = 7.2622$ g/cm^3).

High-temperature X-ray diffraction data show that, at $T = 763 \pm 5$ K, the low-temperature, hexagonal phase transforms into a cubic phase with a lattice parameter $a = 6.0672$ Å (sp. gr. $Pa\bar{3}$, $Z = 4$).

The phase transformation is reversible.

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