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New data on the composition of the crystalline phases in the Cu–Te–O system

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With the help of X-ray microanalysis and X-ray analysis new data about the composition of the crystal phase in the Cu–Te–O system have been obtained. The data from the X-ray microanalysis were treated by the method of the number of the oxygen atoms, and the chemical formulae of the crystal phases were evaluated. The following phases were established: the real composition of the stoichiometric composition $2TeO_2 \cdot CuO$ corresponds to the crystalline phase $5TeO_2 \cdot 2CuO$ with variable composition in the limits from $7TeO_2 \cdot 3CuO$ to $11TeO_2$ $4CuO$ with X-ray data presented as $2TeO_2 \cdot CuO$ phase. The composition $TeO_2 \cdot CuO$ corresponds to a crystalline phase from $TeO_2 \cdot CuO$ to $6TeO_2 \cdot 5CuO$. From a melt of $TeO_2 \cdot CuO$ composition overcooled and crystallized is formed $5CuO \cdot 2TeO_2$. At a given composition $3CuO \cdot TeO_2$ or $3CuO \cdot TeO_3$ corresponds to the crystalline phase $5CuO \cdot 2TeO_3$ with two polymorphic modifications — cubic and tetragonal. The X-ray data obtained in the present investigation and those in literature are accepted to correspond to two polymorphic forms.

1. Introduction

During the study of the phase equilibrium in the Cu_2O–CuO–TeO_2 system [1–3] it was established that quenched melts and glasses form the following crystalline phases: TeO_2, Cu_2O, CuO, $2TeO_2 \cdot CuO$, $TeO_2 \cdot CuO$, as well as one new phase "X" which corresponds to the $3CuO \cdot TeO_3$ phase according to X-ray data after Hostachy *et al.* [4]. Moreover, it was established that the "X" phase was formed when the synthesis was performed in an inert medium or under vacuum. In these cases free Cu_2O was crystallized from CuO-rich compositions. The method of triangulation of possible quasibinary sections in the CuO–TeO_2 system has been used [5] in the range of oxide phases and conclusions about their synthesis have been drawn. At the same time the formation of ternary compounds between Cu_2O, CuO and TeO_2 was not confirmed contrary to earlier suggestions [6].

The aim of the present investigation was to establish the real composition of the crystalline phases in the system, based on data X-ray microanalysis. Taking into account the possibility of oxide reduction processes, the complex phase equilibrium in the system, and the contradictory data in the literature about the compositions of the crystalline phases formed in it.

2. Experimental details

CuO (reagent grade), TeO_2 (99.9%) and TeO_3 (reagent grade) were used as starting raw materials for the synthesis. Compositions corresponding to the stoichiometric relations $2TeO_2 \cdot CuO$, $TeO_2 \cdot CuO$, $3CuO \cdot TeO_3$, $3CuO \cdot TeO_2$, $5CuO \cdot 2TeO_2$, $5CuO \cdot 2TeO_3$ were synthesized. The specimens were produced by two methods: (a) solid state synthesis between the starting oxides (regime A) and (b) by the melting and consequent crystallization (regime B). The synthesis of the compositions was controlled by X-ray powder specimens, apparatus DRON and TuR-M-61 ($CuK\alpha$-radiation, nickel filter) and the composition of the crystalline phases was determined by X-ray microanalyser (Philips).

The results of the spectral analyses were treated using computer methods. The chemical formulae were evaluated on the basis of the oxygen method, as well as the data about the chemical composition of the crystalline phases.

3. Results and discussion

In Table I the given stoichiometric ratios and the conditions of thermal treatment are presented, and in Table II the characteristic X-ray data of known crystalline phases according to the literature are given. In Fig. 1 the morphological peculiarities of the crystalline phases are given. The results obtained of the chemical composition of the crystalline phase in Cu–Te–O system show that from a given stoichiometric composition $2TeO_2 \cdot CuO$ crystallizes a phase with variable composition of the crystalline individuals in the limits from $7TeO_2 \cdot 3CuO$ to $11Te_2 \cdot 4CuO$. It is obvious that these results allow the X-ray diffraction data assigned to the phase with $2TeO_2 \cdot CuO$ composition (Table II) to correspond to phase ratio $TeO_2 \cdot CuO$ from 7 : 3 to 11 : 4 with variable composition from 70 to 73.3% TeO_2.

At given stoichiometric composition $TeO_2 \cdot CuO$ and a synthesis carried out by solid phase interaction at temperatures below 600° C (regime A) data from the X-ray microanalysis show a deviation from the

TABLE I Composition of crystal phases in the Cu-Te-O system

Composition number	Given stoichiometric composition	Composition of the crystal phases from X-ray microanalysis data	Regime of crystallization
1	$2TeO_2 \cdot CuO$	$5TeO_2 \cdot 2CuO$(s.s.) from $7TeO_2 \cdot 3CuO$ to $11TeO_2 \cdot 4CuO$	regime A at 600° C regime B — from a melt (680° C)
2	$TeO_2 \cdot CuO$	From $TeO_2 \cdot CuO$ to $6TeO_2 \cdot 5CuO$ (s.s.)	regime A at 600° C
3	$TeO_2 \cdot CuO$	$5CuO \cdot 2TeO_2$	regime B — from a melt (1000° C) and overcooled and crystallization at 630° C
4	$3CuO \cdot 2TeO_2$	$CuO \cdot TeO_2 + 5CuO \cdot 2TeO_2$	regime A at 520° C
5	$3CuO \cdot TeO_2$	$5CuO \cdot 2TeO_3$	regime A at 720° C
6	$3CuO \cdot TeO_3$	$5CuO \cdot 2TeO_3$	regime A at 720° C
7	$3CuO \cdot TeO_3$	$5CuO \cdot 2TeO_3$	regime B at 800° C
8	$5CuO \cdot 2TeO_3$	$5CuO \cdot 2TeO_3$	regime A at 720° C regime B at 800° C
9	$5CuO \cdot 2TeO_2$	$5CuO \cdot 2TeO_3$	regime A at 720° C regime B at 800° C

Regime A — solid state synthesis between the starting oxides.

TABLE II X-ray data for the phases in Cu–Te–O system

$11TeO_2 \cdot 4CuO$ to $7TeO_2 \cdot 3CuO$ (s.s.)† or $2TeO_2 \cdot CuO$ [1, 2, 3, 10] monoclinic [1, 10, †] $a = 0.6869 \pm 0.0003$ nm $b = 0.9324 \pm 0.0006$ nm $c = 0.7608 \pm 0.0006$ nm $\beta = 109.08 \pm 0.03°$ Interplanar spacings [1, 10, 11]* and [1]*				$TeO_2 \cdot CuO$ to $7TeO_2 \cdot 6CuO$ (s.s.)† or $TeO_2 \cdot CuO$ [1, 2, 3] orthorhombic [1, †] $a = 0.7604 \pm 0.0006$ nm $b = 1.2705 \pm 0.0006$ nm $c = 0.5837 \pm 0.0004$ nm Interplanar spacings [1, 11]*				$CuO \cdot TeO_3$ ($CuTeO_4$) orthorhombic [7] $a = 0.55$ nm $b = 1.0327$ nm $c = 0.4704$ nm		$5CuO \cdot 2TeO_3$† or $3CuO \cdot TeO_3(Cu_3TeO_6)$ cubic [4, 8, 9] $a = 0.9537$ nm [8] Interplanar spacings [4, 8]* and [4]*				$5CuO \cdot 2TeO_3$† tetragonal† Interplanar spacings [†] (Fig. 5)			
I	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)
30	0.6485*	10	0.2223	40	0.634	40	0.2620	40	0.1859	35	0.471*	<2	0.1323	28	0.477	9	0.1322
80	0.4654	20	0.2164	40	0.530	40	0.2547	40	0.1850	10	0.389	2	0.1298	10	0.389	5	0.1319
60	0.3793	30	0.2091	40	0.487	40	0.2505	40	0.1831	10	0.337	6	0.1274	13	0.337	2	0.1297
30	0.3648	20	0.2054	60	0.435	40	0.2436	40	0.1806	100	0.275	2	0.1211	2	0.282	1	0.1292
30	0.3586	30	0.2034	40	0.429	40	0.2402	40	0.1789	1	0.254	6	0.1192	100	0.275	9	0.1273
20	0.3429	10	0.1990	40	0.380	40	0.2354	40	0.1766	40	0.238	2	0.1174	2	0.254	5	0.1270
80	0.3348	10	0.1960	40	0.374	40	0.2330	40	0.1763	2	0.224	6	0.1570	25	0.238	1	0.1210
10	0.3243	10	0.1908	40	0.363	60	0.2278	40	0.1741	6	0.213	2	0.1400	8	0.213	9	0.1192
20	0.3199	10	0.1870	60	0.343	40	0.2225	40	0.1738	8	0.203	4	0.1240	7	0.203	4	0.1190
70	0.3111	20	0.1844	40	0.326	40	0.2183	40	0.1732	13	0.1947	<2	0.1109	13	0.1947	4	0.1173
100	0.3064	10	0.1822	60	0.318	40	0.2147	40	0.1720	10	0.1869	10	0.1094	10	0.1870	2	0.1170
30	0.2932	10	0.1798	40	0.312	40	0.2038	80	0.1716	<2	0.1741	<2	0.1080	2	0.1739	8	0.1156
50	0.2844	20	0.1763	80	0.309	40	0.1990	80	0.1711	40	0.1686	10	0.1066	45	0.1686	4	0.1152
50	0.2796	40	0.1718*	60	0.293	40	0.1985	40	0.1690	<2	0.1636	2	0.1053	13	0.1588	2	0.1139
70	0.2744	40	0.1704	40	0.2915	40	0.1926	40	0.1670	8	0.1589	4	0.1040	9	0.1583	6	0.1122
<1	0.2481	40	0.1679	100	0.2846	40	0.1916	40	0.1662	4	0.1547	2	0.1028	3	0.1543	3	0.1120
10	0.2438	40	0.1675	90	0.2841	40	0.1901	40	0.1631	4	0.1508	2	0.1016		0.1539	12	0.1092
10	0.2383	40	0.1655	40	0.2786	40	0.1890	40	0.1625	6	0.1471	<2	0.1005	8	0.1505	8	0.1088
10	0.2351	40	0.1647	40	0.2662	40	0.1883			30	0.1437	2	0.9836	6	0.1502		
10	0.2244	40	0.1634	40	0.2650	40	0.1875			4	0.1406	6	0.0973	6	0.1469		
		40	0.1625							8	0.1376	2	0.0963		0.1465		
										<2	0.1349*	4	0.0953	35	0.1436		
												2	0.0944		0.1433		
														4	0.1405		
														3	0.1402		
														12	0.1375		
														5	0.1371		

*Composition and interplanar spacings from corresponding reference.

†Composition and interplanar spacings from current work.

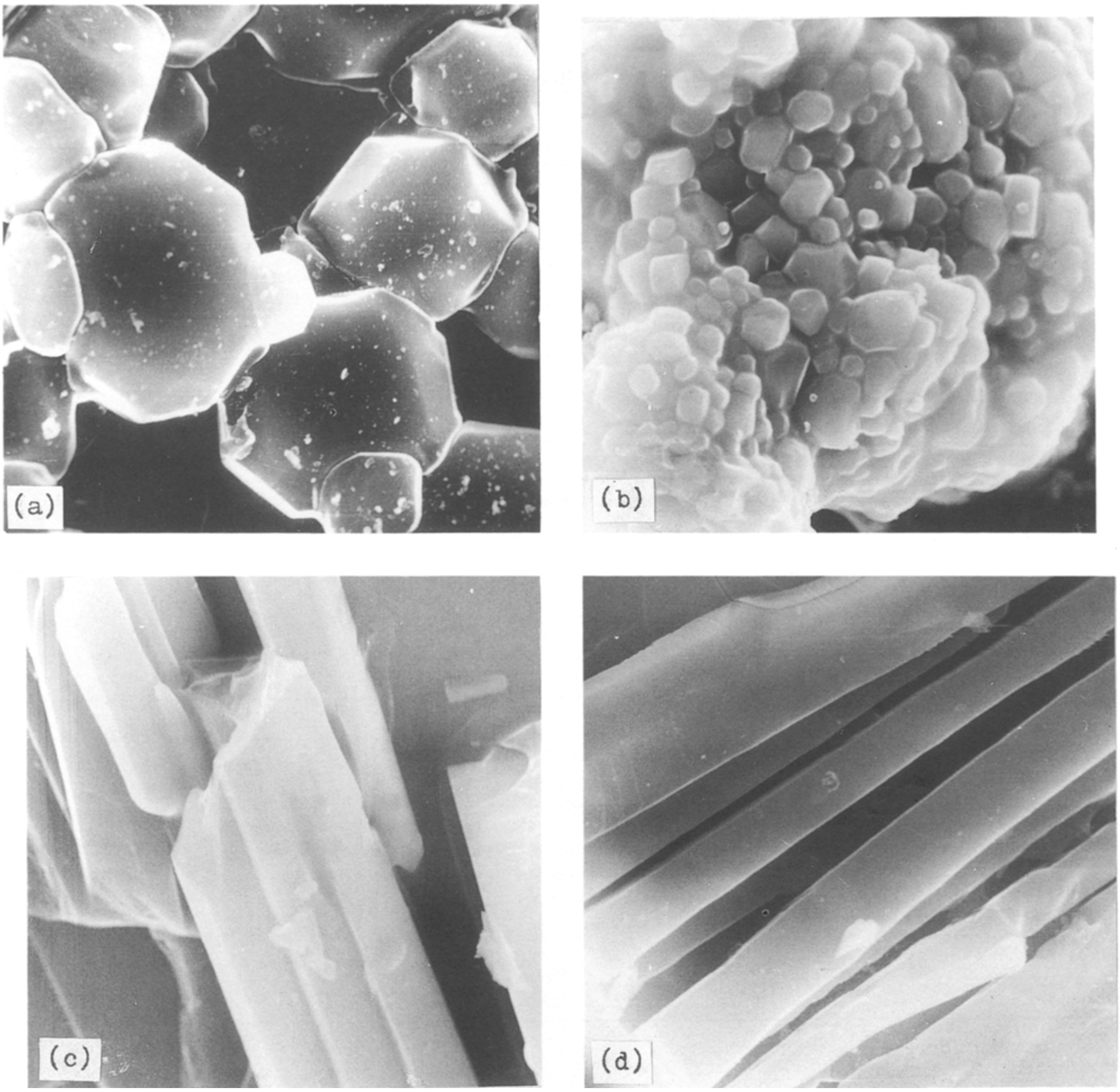

Figure 1 Total appearance of the crystalline phases in the Cu–Te–O system. Scanning electron microscopy. Magnification 470 ×: (a) monocrystals of $5CuO \cdot 2TeO_3$ in the $3CuO \cdot TeO_3$ composition, (b) crystalline unit of $5CuO \cdot 2TeO_3$, (c) stretched monoclinic–prismatic crystals of phase with variable composition ($11TeO_2 \cdot 4CuO$–$7TeO_2 \cdot 3CuO$) in $2TeO_2 \cdot CuO$ composition, (d) stretched prismatic crystals of phase with variable composition ($TeO_2 \cdot CuO$–$6TeO_2 \cdot 5CuO$) in $TeO_2 \cdot CuO$ composition.

assigned one. The composition of the crystalline individuals changes in narrow limits from $TeO_2 \cdot CuO$ to $6TeO_2 \cdot 5CuO$. In the cases when the synthesis was performed by melting and following crystallization above 600° C (regime B) that a significant deviation from the given stoichiometric composition was found. According to the X-ray data, the product corresponds to the $3CuO \cdot TeO_3$ [4] phase, and the data from X-ray microanalysis show the existence of a glassy phase (Fig. 2), rich in TeO_2 (76 to 77%) and crystalline individuals with composition corresponding to TeO_2: CuO 2 : 5 radio (Fig. 2, Table III).

The consecutive synthesis of stoichiometric composition $3CuO \cdot TeO_2$ and $3CuO \cdot TeO_3$ show that it formed only one crystalline phase whose diffraction pictures correspond to the X-ray data in Table II

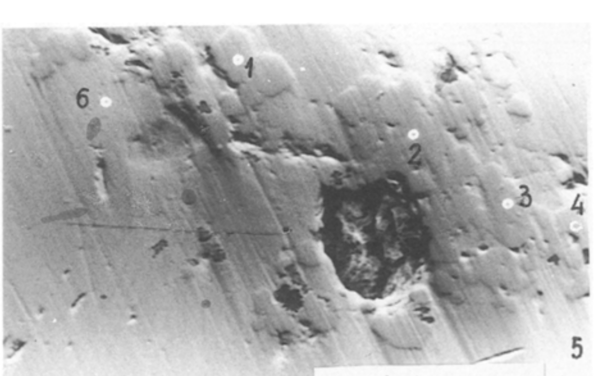

Figure 2 Analysed points in $TeO_2 \cdot CuO$ composition from a melt crystallized at 630° C for 1 h (Table III). Magnification 235 x. Scanning electron microscopy.

TABLE III Chemical composition at the analysed points in a composition $CuO \cdot TeO_2$ from a melt (1000° C) crystallized at 630° C, 1 h (Fig. 2) from X-ray microanalysis data

Analysis points	Composition (%)		Crystal chemical formula
	$\frac{Cu}{CuO}$	$\frac{Te}{TeO_2}$	
1	$\frac{45.497}{56.954}$	$\frac{34.416}{43.047}$	$Cu_{5.13}Te_{1.93}O_9(5CuO \cdot 2TeO_2)$
2	$\frac{45.600}{57.082}$	$\frac{34.313}{42.919}$	$Cu_{5.14}Te_{1.93}O_9(5CuO \cdot 2TeO_2)$
3	$\frac{44.821}{56.107}$	$\frac{35.093}{43.893}$	$Cu_{5.06}Te_{1.97}O_9(5CuO \cdot 2TeO_2)$
4	$\frac{44.887}{56.190}$	$\frac{35.027}{43.811}$	$Cu_{5.06}Te_{1.97}O_9(5CuO \cdot 2TeO_2)$
5	$\frac{19.251}{24.099}$	$\frac{60.683}{75.902}$	glassy phase
6	$\frac{18.494}{23.150}$	$\frac{61.442}{76.851}$	glassy phase

TABLE IV Chemical composition of the analysed crystals in a composition $3CuO \cdot TeO_3$ crystallized from a melt (Fig. 3) from X-ray microanalysis data

Analysis points	Composition (%)		Crystal chemical formula
	$\frac{Cu}{CuO}$	$\frac{Te}{TeO_3}$	
1	$\frac{42.127}{52.734}$	$\frac{34.346}{47.266}$	$Cu_{4.96}Te_{2.01}O_{11}(5CuO \cdot 2TeO_3)$
2	$\frac{42.127}{52.734}$	$\frac{34.346}{47.266}$	$Cu_{4.96}Te_{2.01}O_{11}(5CuO \cdot 2TeO_3)$
3	$\frac{42.609}{53.339}$	$\frac{33.907}{46.662}$	$Cu_{5.03}Te_{1.99}O_{11}(5CuO \cdot 2TeO_3)$
4	$\frac{42.600}{53.327}$	$\frac{33.916}{46.674}$	$Cu_{5.03}Te_{1.99}O_{11}(5CuO \cdot 2TeO_3)$

TABLE V Chemical composition of the analysed crystals in a composition $5CuO \cdot 2TeO_3$, crystallized at solid-state reaction at 720° C (Fig. 4) from X-ray microanalysis data

Analysis points	Composition (%)		Crystal chemical formula
	$\frac{Cu}{CuO}$	$\frac{Te}{TeO_3}$	
Fig. 3a			
1	$\frac{37.253}{46.633}$	$\frac{38.780}{53.368}$	$Cu_{1.96}Te_{1.01}O_5(2CuO \cdot TeO_3)$
2	$\frac{41.486}{51.933}$	$\frac{34.929}{48.068}$	$Cu_{4.87}Te_{2.04}O_{11}(5CuO \cdot 2TeO_3)$
3	$\frac{42.284}{52.931}$	$\frac{34.203}{47.070}$	$Cu_{4.98}Te_{2.01}O_{11}(5CuO \cdot 2TeO_3)$
4	$\frac{41.111}{51.464}$	$\frac{35.270}{48.537}$	$Cu_{4.82}Te_{2.06}O_{11}(5CuO \cdot 2TeO_3)$
5	$\frac{42.418}{53.099}$	$\frac{34.081}{46.902}$	$Cu_{5.00}Te_{2.01}O_{11}(5CuO \cdot 2TeO_3)$
Fig. 3b			
1	$\frac{42.928}{53.738}$	$\frac{33.617}{46.263}$	$Cu_{5.07}Te_{1.99}O_{11}(5CuO \cdot 2TeO_3)$
2	$\frac{42.411}{53.090}$	$\frac{34.088}{46.911}$	$Cu_{5.00}Te_{2.00}O_{11}(5CuO \cdot 2TeO_3)$

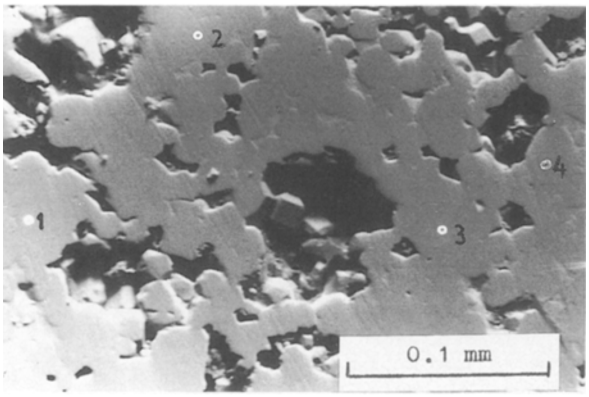

Figure 3 Analysed crystals in a composition $3CuO \cdot TeO_3$ crystallized from a melt (Table IV). Magnification 235 x. Scanning electron microscopy.

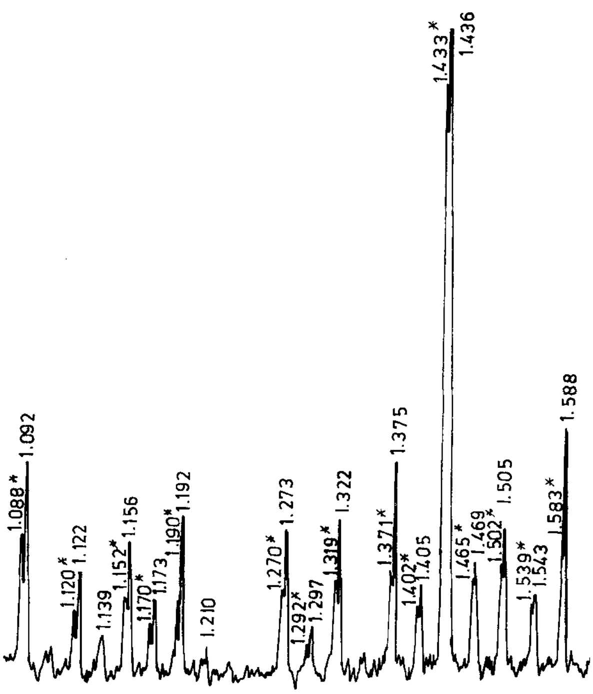

Figure 5 X-ray diffractogram ($\theta = 28$ to 45° at CuKα radiation) of crystalline phase $5CuO \cdot 2TeO_2$, with the appearing additional interplanar distances (∗) in contradiction to reference [4] about the $3CuO \cdot TeO_3$ composition.

presented for the $3CuO \cdot TeO_3$ phase. The real chemical composition in accordance with the data from X-ray microanalysis (Fig. 3, Table IV) corresponds to $5CuO \cdot 2TeO_3$.

The results mentioned above suppose synthesis of specimens corresponding to the stoichiometric radio 5:2 ($CuO:TeO_2$ or TeO_3) by using both regimes of synthesis (Fig. 4, Table V). The results of microanalysis show that in both cases a crystalline phase with $5CuO \cdot 2TeO_3$ composition was formed. Therefore the given interplanar distances for $3CuO \cdot TeO_3$ phase [4] in Table II should be assigned to the crystalline phase with $5CuO \cdot 2TeO_3$ composition. The crystalline phase described and designated by us as the "X" phase [3] possesses composition in accordance with the data of X-ray microanalysis $5CuO \cdot 2TeO_3$.

In the X-ray data, as is seen in Table II, of $3CuO \cdot TeO_3$ [4] there are no interplanar distances with weak intensity and those in the interval $\theta = 28$ to 45° (CuKα) doublet lines [4] (Fig. 5, Table II), found by us in the powder samples. Thus, previous [4] evaluated parameters of the individual unit of $3CuO \cdot TeO_3$ phase which correspond to $5CuO \cdot 2TeO_3$ composition in real phase "X" [3] was assigned a cubic system.

During our optical observations [3] of this phase a weak anisotropic effect was found, which, along with the morphological peculiarities and the habitus allow us to assign it to a tetragonal system. The differences found by us [4] are most probably connected with a polymorph transformation of the crystalline phase with $5CuO \cdot 2TeO_3$ composition. The cubic form of $3CuO \cdot TeO_3$ (in reality $5CuO \cdot 2TeO_3$), [4] is assigned to the structural type of bixbyite $(Mn, Fe)_2O_3$ for which the composition of two polymorphic modifications are also known. The structural differences in the X-ray diffraction picture determined by us [4] for $5CuO \cdot 2TeO_3$ composition most probably are due to the differences in the synthesis conditions.

4. Conclusions

With the help of X-ray microanalysis the real composition was determined of what was previously thought to be $2TeO_2 \cdot CuO$, $TeO_2 \cdot CuO$ and $3CuO \cdot TeO_3$ phases in the system Cu–Te–O (Fig. 6). The composition $2TeO_2 \cdot CuO$ corresponds to the crystalline phase $5TeO_2 \cdot 2CuO$ with variable composition in the limits from $7TeO_2 \cdot 3CuO$ to

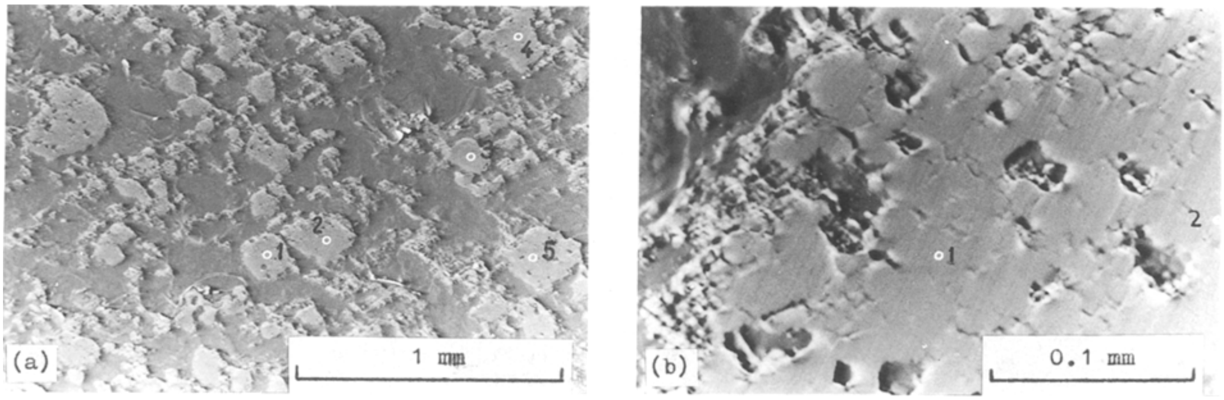

Figure 4 Analysed crystals in a composition $5CuO \cdot 2TeO_3$ crystallized at solid-state reaction at 720° C (Table V). Magnification: (a) 29.4 ×, (b) 235 ×. Scanning electron microscopy.

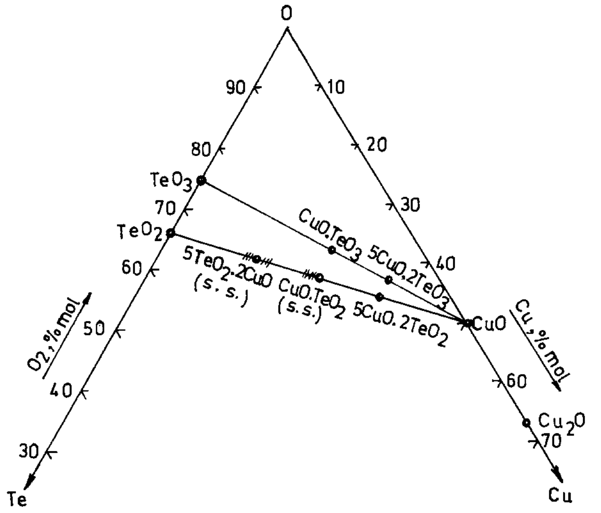

Figure 6 Crystalline phases in the Cu–Te–O system in accordance with the present investigation and reference [7].

$11TeO_2 \cdot 4CuO$ with X-ray data presented as the $2TeO_2 \cdot CuO$ phase.

The composition $TeO_2 \cdot CuO$ corresponds to a crystalline phase with variable composition in narrow limits from $TeO_2 \cdot CuO$ to $5TeO_2 \cdot 6CuO$.

The suggested $3CuO \cdot TeO_3$ phase with which corresponds a crystalline phase with composition $5CuO \cdot 2TeO_3$, as the X-ray data obtained in the present investigation [4] are accepted to correspond to the polymorphic forms – tetragonal and cubic.

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