NEW TERNARY PHASES FROM THE Tb-Cu-Cd: XRD and DSC INVESTIGATIONS

A.I.Horechyy[1], V.V.Pavlyuk[2], O.I.Bodak[2],
J.J.Kozioł[2], **W.Ciesielski[2]**, J.Kapuśniak[2]
[1]Department of Inorganic Chemistry, Ivan Franko Lviv State University, Kyryla and Mefodia str. 6, Lviv, Ukraine
[2]Institute of Chemistry, Pedagogical University of Częstochowa, 42200, Częstochowa, Poland

Isotermal section of the phase diagram of Tb-Cu-Cd system at 570 K was investigated by X-ray method. Four ternary compounds were found in Tb-Cu-Cd system. There is no polymorphic transformation observed for the ternary phase $TbCu_{5-x}Cd_x$ against binary compounds ($GdCu_5$ and $TbCu_5$).
The research of components interaction in the ternary system with terbium, copper and cadmium has not been carried out yet. There are also no literature data on study of crystal structures of ternary compounds for this system. From the most related systems, only La-Ni-Zn [1], partially Ce-Ni-Zn [2,3] and Ce-Cu-Cd [4] were studied earlier. Binary systems Tb-Cu, Tb-Cd are investigated and described in [5] well enough, but there are no diagrams constructed for them. Crystallographic characteristics for the binary compounds of these systems according to [6] are listed in Table 1.
Results of investigation of the isothermal section of Tb-Cu-Cd system at 570 K are presented in this paper.

EXPERIMENTAL

Isothermal section of the phase diagram of Tb-Cu-Cd system have been constructed by X-ray phase analysis of 59 alloys. Purity of the elements were: terbium ~98 wt.%, electrolytic copper 99.99 wt.% and Cd 99.999

wt.%. The samples were arc melted in an argon atmosphere and then annealed at 570 K for 600 h.

X-ray powder patterns were obtained using a DRON-2.0 powder diffractometer with Fe-K_α radiation and the crystal lattice parameters were determined for the whole series of investigated compounds. The terbium phase was chosen for more detailed structural investigation. In this case the X-ray measurements were also performed using SIEMENS X-ray powder diffractometer with Co-K_α radiation. The measurement was carried out at room temperature between 20 and 90 degree in 2θ. Diffraction data were collected with 2θ steps of 0.02 and step times 8-10 s. The XPD data were analyzed with the Rietveld profile refinement method using the DBWS-9006PC program [7]. To confirm the composition of the crystal grain in alloys local spectral analysis was used (SEM "LEITZ-AMR 1600T" with EDX-detector).

RESULTS AND DISCUSSION

The phase diagram of the Tb-Cu-Cd system at 570 K, in range of concentrations of cadmium from 0.0 to 80.0 at.%, is shown in Figure 1. Compositions of alloys and observed phases are given in Table 2.

Four ternary compounds were found in the Tb-Cu-Cd system. Lattice parameters of these compounds are presented in Table 3.

Compound $TbCu_{6-x}Cd_x$ (x=3.5-4) is crystallized in YCd_6 structure type and has a region of homogeneity from 50 to 60 at.% of cadmium. Atom of terbium is occupying positions 24(g) (0 y z, y=0.1919(2), z=0.3059(3)). The same position is occupied by yttrium atom in the YCd_6 structure. Position 16(f) is occupied by atoms of copper only on 65 %. Other positions are occupied by statistic mixture of copper and cadmium.

Compound TbCuCd is crystallized in the same structure type as CeCuCd compound (sp. group P321, CeCuCd structure type). The atomic position are: Ce 1(a) (x=0, y=0, z=0); Cu:1(d) (x=0.33, y=0.67, z=0,5); Cd: 1(f) (x=0.67, y=0.33, z=0,5);

Tb_2CuCd compound is crystallized in $MnCu_2Al$ str. type ($Fm\overline{3}m$ sp.gr.). Atoms of terbium are occupying position 8(c) (x=0.25, y=0.25, z=0.25), atoms of Cu – positions 4(b) (x=0.5, y=0.5, z=0.5), and atoms of cadmium – position 4(a) (x=0, y=0, z=0).

Compound $TbCu_{5-x}Cd_x$ (x=1.2-2.1) is crystallized in the same structure type as a $CeCu_{5-x}Cd_x$ compound (sp. group $F\overline{4}3m$, $AuBe_5$ str. type)[8]. There is no polymorphic transformation observed for the ternary phase $TbCu_{5-x}Cd_x$, against binary compounds ($GdCu_5$ and $TbCu_5$). This result has been obtained by means DSC measurement. The heating and cooling curves have been studied in the temperature interval from 20 °C to 1000 °C for the $TbCu_{3.8}Cd_{1.2}$ alloy. There is only one peak present in these curves, attributed to the melting temperature of ternary phase (810 °C) (Figure 2).

The homogeneity region for $TbCu_{5-x}Cd_x$ and $TbCu_{6-x}Cd_x$ compounds were determined by change of cell's lattice parameters (Figure 3 and Table 4). Formation of the limited solid solutions on the base of Tb-Cu and Tb-Cd binary compounds are observed in this ternary system. The largest solid solution on the binary compound $TbCu_2$ (~8 at.% Cd) is characterized.

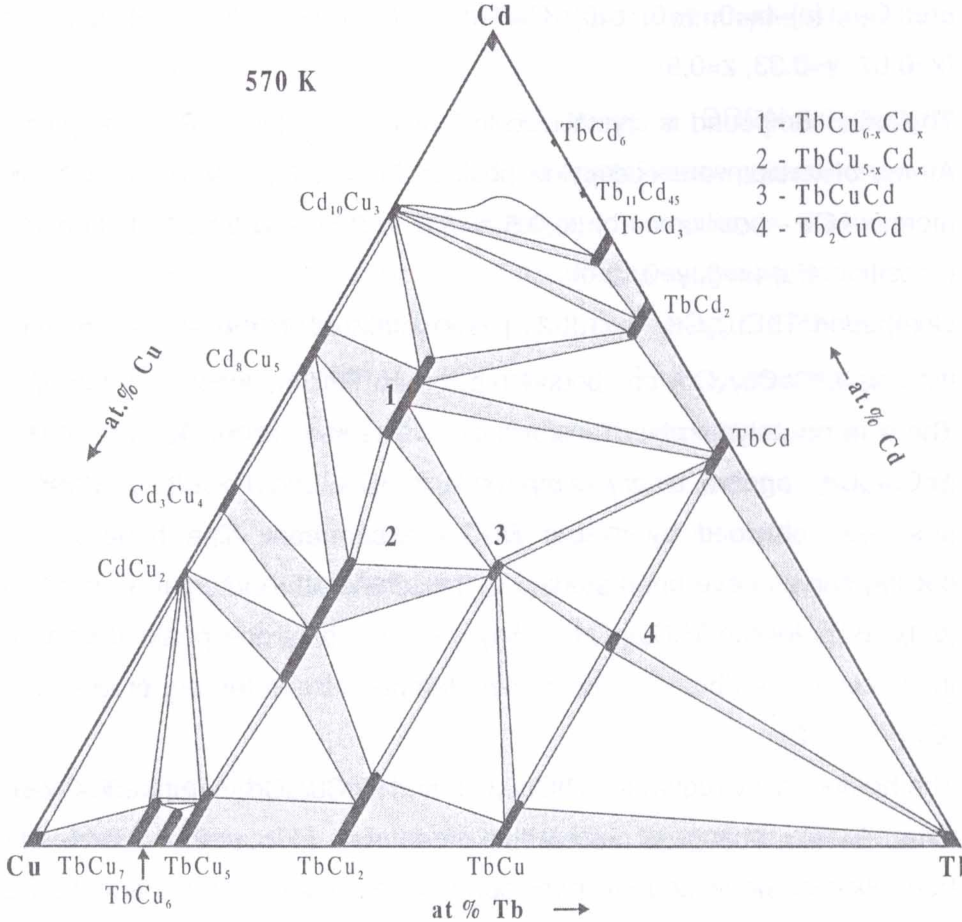

Figure 1. Isothermal section of Tb-Cu-Cd system at 570 K.

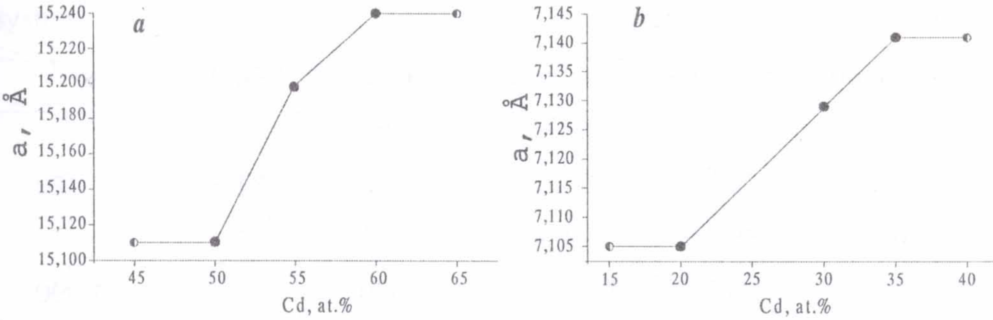

Figure 2. Change of lattice parameters for $TbCu_{6-x}Cd_x$ (x=3.5-4) (*a*) and $TbCu_{5-x}Cd_x$ (x=1.2-2.1) (*b*) compounds.

☒ - samples are not single phases;

● - samples are single phases.

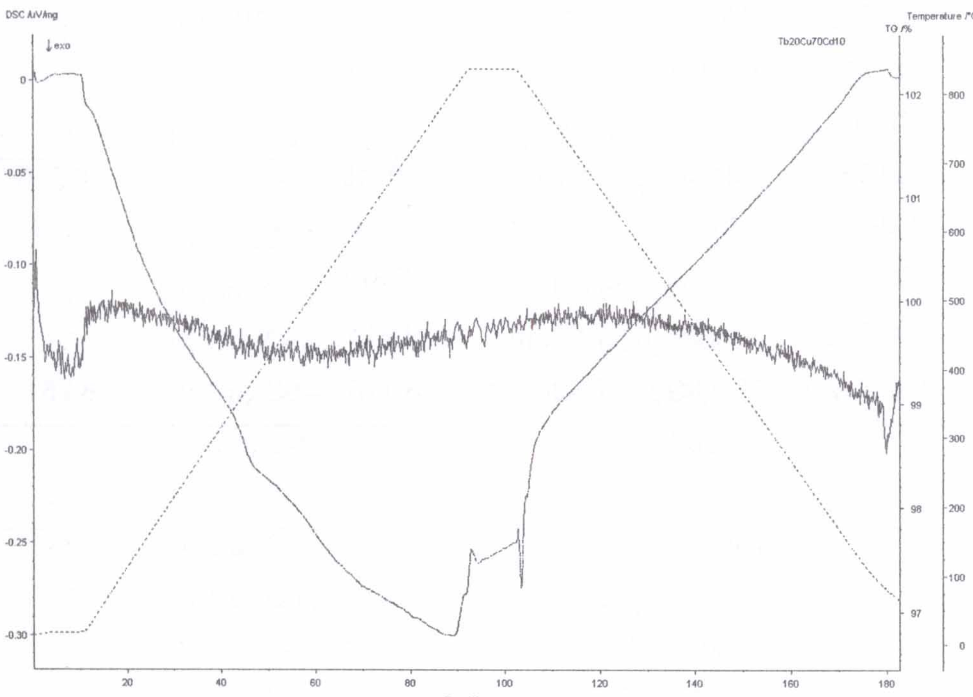

Figure 3. DSC-measurement of the $TbCu_{3.8}Cd_{1.2}$ compound.

Table 1. Crystallographic characteristics of binary compounds of Tb-Cu, Tb-Cd and Cd-Cu systems.

Compound	Str. type	Sp. group	a, Å	b, Å	c, Å
TbCu	CsCl	$Pm\bar{3}m$	3.457		
$TbCu_2$	$CeCu_2$	Imma	4.310	6.825	7.320
$TbCu_5$	$AuBe_5$	$F\bar{4}3m$	7.041		
$TbCu_5$	$CaCu_5$	P6/mmm	5.030		4.090
$TbCu_6$	$CeCu_6$	Pnma	8.02	5.01	10.01
$TbCu_7$	$TbCu_7$	P6/mmm	4.942		4.164
TbCd	CsCl	$Pm\bar{3}m$	3.734		
$TbCd_2$	$CeCd_2$	$P\bar{3}m1$	4.905		3.450
$TbCd_3$	Ni_3Sn	$P6_3/mmc$	6.585		4.925
$TbCd_3$	HgNa	CmCm	6.963	10.970	4.851
$Tb_{11}Cd_{45}$	$Sm_{11}Cd_{45}$	$F\bar{4}3m$	21.550		
$TbCd_6$	YCd_6	Im3	15.494		
$CdCu_2$	$MgNi_2$	$P6_3/mmc$	5.0115		16.210
$CdCu_2$	$MgZn_2$	$P6_3/mmc$	4.96		7.99
Cd_3Cu_4	Cd_3Cu_4	$F\bar{4}3m$	25.871		
Cd_8Cu_5	Cd_8Cu_5	$I\bar{4}3m$	9.615		
$Cd_{10}Cu_3$	Al_5Co_2	$P6_3/mmc$	8.118		8.751

Table 2. Composition and observed phases for alloys of Tb-Cu-Cd system.

№	Composition	Phases
1	$Tb_5Cu_{85}Cd_{10}$	$TbCu_7 + CdCu_2 + Cu$
2	$Tb_5Cu_{75}Cd_{20}$	$TbCu_7 + CdCu_2$
3	$Tb_5Cu_{70}Cd_{25}$	$TbCu_5 + CdCu_2$
4	$Tb_5Cu_{65}Cd_{30}$	$TbCu_{5-x}Cd_x + CdCu_2$
5	$Tb_5Cu_{60}Cd_{35}$	$TbCu_{5-x}Cd_x + CdCu_2 + Cd_3Cu_4$
6	$Tb_5Cu_{55}Cd_{40}$	$TbCu_{5-x}Cd_x + Cd_3Cu_4$
7	$Tb_{10}Cu_{80}Cd_{10}$	$TbCu_7 + TbCu_5 + CdCu_2$
8	$Tb_{10}Cu_{70}Cd_{20}$	$TbCu_{5-x}Cd_x + TbCu_5 + CdCu_2$
9	$Tb_{10}Cu_{60}Cd_{30}$	$TbCu_{5-x}Cd_x + CdCu_2 + Cd_3Cu_4$
10	$Tb_{10}Cu_{50}Cd_{40}$	$TbCu_{5-x}Cd_x + Cd_3Cu_4 + Cd_8Cu_5$
11	$Tb_{10}Cu_{40}Cd_{50}$	$TbCu_{6-x}Cd_x + TbCu_{5-x}Cd_x + Cd_8Cu_5$
12	$Tb_{10}Cu_{30}Cd_{60}$	$TbCu_{6-x}Cd_x + Cd_8Cu_5 + Cd_{10}Cu_3$
13	$Tb_{10}Cu_{20}Cd_{70}$	$TbCu_{6-x}Cd_x + Cd_{10}Cu_3 + TbCd_2$
14	$Tb_{14}Cu_{41}Cd_{45}$	$TbCu_{6-x}Cd_x + TbCu_{5-x}Cd_x + Cd_8Cu_5$
15	$Tb_{14}Cu_{36}Cd_{50}$	$TbCu_{6-x}Cd_x$
16	$Tb_{14}Cu_{31}Cd_{55}$	$TbCu_{6-x}Cd_x$
17	$Tb_{14}Cu_{26}Cd_{60}$	$TbCu_{6-x}Cd_x$
18	$Tb_{14}Cu_{21}Cd_{65}$	$TbCu_{6-x}Cd_x + TbCd_2 + Cd_{10}Cu_3$
19	$Tb_{15}Cu_{80}Cd_5$	$TbCu_7 + TbCu_5$
20	$Tb_{15}Cu_{10}Cd_{75}$	$Cd_{10}Cu_3 + TbCd_3$
21	$Tb_{17}Cu_{68}Cd_{15}$	$TbCu_{5-x}Cd_x + TbCu_5$
22	$Tb_{17}Cu_{63}Cd_{20}$	$TbCu_{5-x}Cd_x$
23	$Tb_{17}Cu_{58}Cd_{25}$	$TbCu_{5-x}Cd_x$
24	$Tb_{17}Cu_{53}Cd_{30}$	$TbCu_{5-x}Cd_x$
25	$Tb_{17}Cu_{48}Cd_{35}$	$TbCu_{5-x}Cd_x$
26	$Tb_{17}Cu_{43}Cd_{40}$	$TbCu_{5-x}Cd_x + TbCu_{6-x}Cd_x$

27	$Tb_{20}Cu_{70}Cd_{10}$	$TbCu_{5-x}Cd_x + TbCu_5 + TbCu_2$
28	$Tb_{20}Cu_{60}Cd_{20}$	$TbCu_{5-x}Cd_x + TbCu_2$
29	$Tb_{20}Cu_{50}Cd_{30}$	$TbCu_{5-x}Cd_x + TbCuCd$
30	$Tb_{20}Cu_{40}Cd_{40}$	$TbCu_{6-x}Cd_x + TbCu_{5-x}Cd_x + TbCuCd$
31	$Tb_{20}Cu_{30}Cd_{50}$	$TbCu_{6-x}Cd_x + TbCuCd + TbCd$
32	$Tb_{20}Cu_{20}Cd_{60}$	$TbCu_{6-x}Cd_x + TbCd_2$
33	$Tb_{20}Cu_{10}Cd_{70}$	$TbCd_2 + Cd_{10}Cu_3$
34	$Tb_{30}Cu_{50}Cd_{20}$	$TbCu_{5-x}Cd_x + TbCuCd + TbCu_2$
35	$Tb_{30}Cu_{40}Cd_{30}$	$TbCu_{5-x}Cd_x + TbCuCd + TbCu_2$
36	$Tb_{30}Cu_{30}Cd_{40}$	$TbCu_{6-x}Cd_x + TbCuCd + TbCd$
37	$Tb_{30}Cu_{20}Cd_{50}$	$TbCu_{6-x}Cd_x + TbCuCd + TbCd$
38	$Tb_{30}Cu_{10}Cd_{60}$	$TbCu_{6-x}Cd_x + TbCd + TbCd_2$
39	$Tb_{33}Cu_{57}Cd_{10}$	$TbCuCd + TbCu_2$
40	$Tb_{33}Cu_{47}Cd_{20}$	$TbCuCd + TbCu_2$
41	$Tb_{33}Cu_{37}Cd_{30}$	$TbCuCd + TbCu_2$
42	$Tb_{33}Cu_{33}Cd_{34}$	$TbCuCd$
43	$Tb_{33}Cu_{27}Cd_{40}$	$TbCu_{6-x}Cd_x + TbCuCd + TbCd$
44	$Tb_{40}Cu_{10}Cd_{50}$	$TbCuCd + TbCu_2 + TbCu$
45	$Tb_{40}Cu_{20}Cd_{40}$	$TbCuCd + TbCu$
46	$Tb_{40}Cu_{30}Cd_{30}$	$TbCuCd + Tb_2CuCd$
47	$Tb_{40}Cu_{40}Cd_{20}$	$TbCuCd + TbCd$
48	$Tb_{40}Cu_{50}Cd_{10}$	$TbCu_{6-x}Cd_x + TbCd$
49	$Tb_{50}Cu_{10}Cd_{40}$	$Tb_2CuCd + TbCu$
50	$Tb_{50}Cu_{20}Cd_{30}$	$Tb_2CuCd + TbCu$
51	$Tb_{50}Cu_{25}Cd_{25}$	Tb_2CuCd
52	$Tb_{50}Cu_{30}Cd_{20}$	$Tb_2CuCd + TbCd$
53	$Tb_{50}Cu_{40}Cd_{10}$	$Tb_2CuCd + TbCd$
54	$Tb_{60}Cu_{30}Cd_{10}$	$Tb_2CuCd + TbCu + Tb$
55	$Tb_{60}Cu_{20}Cd_{20}$	$Tb_2CuCd + Tb$

56	$Tb_{60}Cu_{10}Cd_{30}$	Tb_2CuCd + TbCd + Tb
57	$Tb_{70}Cu_{20}Cd_{10}$	Tb_2CuCd + TbCu + Tb
58	$Tb_{70}Cu_{10}Cd_{20}$	Tb_2CuCd + TbCd + Tb
59	$Tb_{80}Cu_{10}Cd_{10}$	Tb_2CuCd + Tb

Table 3. Crystallographic characteristics for the ternary compounds of the Tb-Cu-Cd systems.

Compound	Str. type	Space group	a, Å	c, Å
$TbCu_{6-x}Cd_x$ (x=3.5 - 4.0)	YCd_6	$Im\bar{3}$	15.109(10) – 15.238(13)	
$TbCu_{5-x}Cd_x$ (x=1.2 - 2.1)	$AuBe_5$	$F\bar{4}3m$	7.105(4) - 7.141(6)	
Tb_2CuCd	$MnCu_2Al$	$Fm\bar{3}m$	7.050(7)	
TbCuCd	TbCuCd	P312	4.978(7)	3.354(9)

Table 4. Lattice parameters for $TbCu_{6-x}Cd_x$ (x=3.5-4), $TbCu_{5-x}Cd_x$ (x=1.2-2.1) solid solutions.

$TbCu_{6-x}Cd_x$ (x=3.5-4.0)			$TbCu_{5-x}Cd_x$ (x=1.2-2.1)		
x	at.% Cd	a, Å	x	at.% Cd	a, Å
3.2	45*	15.109(10)	0.9	15*	7.105(4)
3.5	50	15.109(10)	1.2	20	7.105(4)
3.8	55	15.199(8)	1.8	30	7.129(6)
4.2	60	15.238(13)	2.1	35	7.141(6)
4.4	65*	15.238(13)	2.4	40*	7.141(6)

*samples are not single phases.

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