Supplemental Materials

Table S1 Crystal parameters in Cu-Sb-Te system.

Phase	Strukturbericht designation	Prototype	Pearson symbol	Space group	Ref.
(Cu)	A1	Cu	cF4	$Fm\bar{3}m$	[18]
(Sb)	A7	As	hR2	$R\bar{3}m$	[18, 23]
(Te)	A8	Se	hP3	$P3_121$	[23]
Cu-Sb system					
β-Cu_3Sb	$D0_3$	BiF_3	cF16	$Fm\bar{3}m$	[18]
γ-Cu_4Sb	A7	Mg	hP2	$P6_3/mmc$	[18, 19]
δ-$Cu_{78}Sb_{20}$	-	$Cu_{78}Sb_{21}$	hP98	$P6_3/mmc$	[19]
ε-Cu_3Sb	-	Cu_3Ti	oP8	$Pmmn$	[19]
η-Cu_2Sb	C38	Cu_2Sb	tP6	P_4/nmm	[19]
ζ-$Cu_{10}Sb_3$	-	$Cu_{10}Sb_3$	hP26	$P\bar{3}$	[19]
Sb-Te system					
δ-(Sb, Te)	-	-	-	$P\bar{3}m1$	[23]
γ-(Sb, Te)	A7	As	hR2	$R\bar{3}m$	[23]
Sb_2Te_3	C33	Bi_2Te_3	hR5	$R\bar{3}m$	[23]
Cu-Te system					
A-Cu_2Te	-	-	cF12	$Fd3m$	[26, 46]
B-Cu_2Te	-	-	hP6	$P6/mmm$	[46, 47]
C-Cu_2Te	-	-	hP*	-	[38, 55]
			o**	-	[26, 46]
D-Cu_2Te	-	-	o**	-	[29, 46]
E-Cu_2Te	-	-	o**	-	[46, 47]
F-$Cu_{13+x}Te_7$	-	-	o**	-	[29, 46]
G-$Cu_{13+x}Te_7$	-	-	o**	-	[26, 46, 47]
H-$Cu_{9\pm x}Te_5$	-	-	hP72	$P3m1$	[26, 46, 47]
J-$Cu_{9\pm x}Te_5$	-	-	hP*	-	[26, 46]
K-Cu_7Te_4	-	-	hP22	$P3m1$	[26, 46]
K-Cu_7Te_4	-	-	hP22	-	[55]
Φ*	-	-	-	-	[26, 29]
N_1-$Cu_{3-x}Te_2$	-	-		-	[29, 48]
N_2-$Cu_{3-x}Te_2$	-	-		$P4/nmm$	[29, 43]
N_2-$Cu_{3-x}Te_2$	-	-		-	[41]
N_3-$Cu_{3-x}Te_2$	-	-		-	[29, 41]
N_3-$Cu_{3-x}Te_2$	-	-		$Pmmm$	[48]
Cu_4Te_3	-	-	-	-	[27, 41]
CuTe	B19	AuCd	oP4	$Pmmm$	[46]
$CuTe_2$	-	-	cP12	$Pa3$	[41]

Where '-' and '*' mean there exists no available data.

Table S2 Nominal compositions of as-cast alloys, phases identified by EDS/WDS, and thermal characterization of representative alloys by DSC. All compositions are given in at.%, and the primary phases are marked with **bold** texts.

Alloy	Nominal Composition		Observed Phases	Phase Composition measured by EDS		Phase Composition measured by WDS		T_{DSC}/°C	Invariant reaction
	Cu	Te		Cu	Te	Cu	Te		
1	76.63	15.03	β-Cu_3Sb	75.1	0.0	78.4	0.7		
			ζ-Cu_2Te	64.7	30.2	67.3	31.6		
			(Cu)	93.4	1.4	W95.3	0.1		
			L_1	67.0	32.4	71.1	24.0		
			L_2	88.1	5.9	85.2	8.1		
2	81.20	18.80	ζ-Cu_2Te	65.3	34.7	-	-		

			(Cu)	99.8	0.2	-	-		
3	90.00	5.00	**ζ-Cu_2Te**	61.4	36.0	-	-		
			β-Cu_3Sb	73.8	1.1	-	-		
			(Cu)	95.3	3.3	-	-		
4	80.00	5.00	**ζ-Cu_2Te**	61.6	34.5	-	-		
			(Cu)	97.9	1.4	-	-	645	
			β-Cu_3Sb	74.5	0.7	-	-		$L_2 \rightarrow$ (Cu) + ζ-Cu_2Te + β-Cu_3Sb (E_1)
5	83.33	1.67	**(Cu)**	95.2	0.0	-	-		
			β-Cu_3Sb	64.4	0.0	-	-	646	
			ζ-Cu_2Te	60.1	35.5	-	-		
6	72.07	11.27	**ζ-Cu_2Te**	61.7	33.6	66.6	30.3	658	
			β-Cu_3Sb	71.5	0.0	75.4	1.6		L_1 + ζ-Cu_2Te + β-$Cu_3Sb \rightarrow$ τ-$Cu_2Sb_xTe_{1-x}$ (P_1)
7	67.50	7.50	**τ-$Cu_2Sb_xTe_{1-x}$**	61.0	16.0	66.3	10.8	654	
			η-Cu_2Sb	60.4	4.2	69.8	2.1		
8	60.00	5.00	**β-Cu_3Sb**	77.3	1.8	-	-		
			ζ-Cu_2Te	61.6	38.0	-	-		
			(Sb)	3.1	0.0	-	-		
9	50.00	10.00	**τ-$Cu_2Sb_xTe_{1-x}$**	-	-	64.8	8.6	578	L_1 + β-$Cu_3Sb \rightarrow$ τ-$Cu_2Sb_xTe_{1-x}$ + η-Cu_2Sb (U_1)
			η-Cu_2Sb	68.3	0.0	65.9	1.4		
			(Sb)	2.0	0.0	-	-	515	
			Eutectic area	-	-	40.3	4.1		
10	50.00	5.00	**τ-$Cu_2Sb_xTe_{1-x}$**	-	-	65.8	21.9		L_1 + τ-$Cu_2Sb_xTe_{1-x} \rightarrow$ ζ-Cu_2Te + η-Cu_2Sb (U_4)
			η-Cu_2Sb	68.8	0.5	66.0	1.1	515	
			(Sb)	4.4	2.8	-	-		
			Eutectic area	-	-	40.7	4.4		
11	55.00	5.00	**τ-$Cu_2Sb_xTe_{1-x}$**	-	-	65.9	20.2		
			η-Cu_2Sb	68.6	31.4	65.9	1.1		
			(Sb)	4.3	2.2	-	-		
			Eutectic area	-	-	40.4	3.6		
12	30.00	10.00	**ζ-Cu_2Te**	49.1	24.9	-	-		
			(Sb)	0.8	3.5	-	-		
			Eutectic area	24.1	12.0	22.8	11.0		
13	45.00	15.00	**ζ-Cu_2Te**	58.6	34.5	-	-		
			(Sb)	0.3	4.8	-	-		
			η-Cu_2Sb	67.3	0.1	-	-		
			Eutectic area	39.3	6.6	37.5	4.3		
14	35.00	3.33	**(Sb)**	1.1	0.0	1.0	0.1		
			ζ-Cu_2Te	-	-	-	-		
			η-Cu_2Sb	67.4	0.0	66.0	1.0		
			Eutectic area	43.3	5.5	40.0	4.0		
15	39.50	5.65	**(Sb)**	2.2	0.0	-	-	574	L_1 + β-$Cu_3Sb \rightarrow$ τ-$Cu_2Sb_xTe_{1-x}$ + η-Cu_2Sb (U_1)
			ζ-Cu_2Te	66.5	28.0	-	-		
			η-Cu_2Sb	67.7	0.6	-	-	≈494	L → ζ-Cu_2Te + (Sb) + η-Cu_2Sb (E_2)
			Eutectic area	41.3	0.9	39.8	4.2		
16	41.50	5.30	**η-Cu_2Sb**	69.7	0.0	-	-		
			(Sb)	4.9	0.0	-	-		
			ζ-Cu_2Te	65.7	32.3	-	-		
			Eutectic area	43.0	1.3	37.9	5.0		

17	10.00	20.00	**(Sb)**	2.7	6.9	0.5	0.0		
			δ-(Sb, Te)	4.2	23.4	1.8	27.9	≈505	L +(Sb) → δ-(Sb, Te) + ε-Cu_2Te (U_6)
			ζ-Cu_2Te	-	-	-	-		
			Eutectic area	22.8	14.1	22.3	13.9		
18	20.00	22.00	**(Sb)**	0.9	0.0	-	-		
			Eutectic area	26.7	33.2	-	-		
19	15.00	26.00	**(Sb)**	0.7	8.0	-	-		
			δ-(Sb, Te)	1.0	36.7	-	-		
			ε-Cu_2Te	-	-	-	-		
			Eutectic area	24.9	22.8		-		
20	10.00	25.00	**(Sb)**	5.7	10.6	-	-		
			δ-(Sb, Te)	0.0	24.4	-	-		
			ε-Cu_2Te	-	-	-	-		
			Eutectic area	22.2	39.7	26.5	39.06		
21	5.00	30.00	**δ-(Sb, Te)**	0.2	26.6	-	-		
			ε-Cu_2Te	-	-	-	-		
22	15.00	30.00	**δ-(Sb, Te)**	2.0	19.4	5.7	18.1		
			ε-Cu_2Te	-	-	-	-		
			Eutectic area	21.8	36.5	21.9	31.4		
23	10.00	40.00	**γ-(Sb, Te)**	1.0	42.8	-	-		
			ε-Cu_2Te	66.9	31.6	-	-		
			Eutectic area	22.2	39.8	-	-		
24	15.00	40.00	**γ-(Sb, Te)**	2.6	44.8	2.8	42.2		
			ε-Cu_2Te	-	-	-	-		
			Eutectic area	25.7	39.6	26.2	38.0		
25	40.00	35.00	**ε-Cu_2Te**	69.9	25.8	63.2	36.8		
			γ-(Sb, Te)	9.0	46.3	2.2	15.6		
			δ-(Sb, Te)	-	-	-	-		
			Eutectic area	19.8	39.8	24.0	34.7		
26	25.00	35.00	**γ-(Sb, Te)+ε−Cu_2Te**	27.7	40.5	-	-		
			γ-(Sb, Te)	1.8	32.3	-	-	482	L + γ-(Sb, Te) → δ-(Sb, Te) + ε-Cu_2Te (U_7)
			δ-(Sb, Te)	-	-	-	-		
27	30.00	40.00	**γ-(Sb, Te)+ε−Cu_2Te**	25.5	41.0	30.9	39.4	496	
								526	L + Sb_2Te_3 → γ-(Sb, Te) + ε-Cu_2Te (U_3)
28	35.00	45.00	**ε−Cu_2Te+Sb_2Te_3**	42.0	43.8	47.1	41.3		
			Sb_2Te_3	0.3	60.8	-	-		
			Cu_4Te_3	-	-	-	-		
			Eutectic area	-	-	26.6	41.4		
29	40.00	45.00	**ε-Cu_2Te**	-	-	63.6	36.4		
			Sb_2Te_3	2.7	59.8	-	-		
			Cu_4Te_3	55.4	43.4	59.1	40.9		
			Eutectic area	39.0	43.9	37.3	45.4		
30	55.00	40.00	**ε-Cu_2Te**	61.9	35.2	-	-		
			Sb_2Te_3	-	-	-	-		
			Cu_4Te_3	-	-	-	-		
			Eutectic area	40.6	44.7	33.2	47.0		
31	45.00	50.00	**Cu_4Te_3**	55.3	43.6	-	-		

			CuTe	48.4	50.4	-	-		
			Sb_2Te_3	7.1	58.4	-	-		
32	30.00	65.00	**CuTe**	47.4	52.6	48.7	51.4		
			(Te)	1.8	92	-	-		
			Sb_2Te_3	-	-	-	-		
			Eutectic area	31.2	63.9	26.3	67.7		
33	15.00	80.00	**(Te)**	0.9	99.1	-	-		
			CuTe	50.3	49.7	-	-		
			Sb_2Te_3	-	-	-	-		
			Eutectic area	29.4	66.5	26.2	67.9		
34	22.50	70.00	**(Te)**	1.0	93.0	-	-		
			CuTe	46.5	53.3	-	-	≈338	L → CuTe + (Te) + Sb_2Te_3 (E_3)
			Sb_2Te_3	-	-	-	-		
			Eutectic area	21.8	72.4	23.1	69.3		
35	10.00	80.00	**Sb_2Te_3**	0.0	72.8	1.1	65.4		
			(Te)	0.0	99.4	0.2	99.8		
			CuTe	47.1	52.7	-	-		
			Eutectic area	-	-	27.2	66.3		
36	15.00	70.00	**Sb_2Te_3**	2.1	62.8	-	-		
			CuTe	48.7	48.9	-	-		
			(Te)	1.1	98.3	-	-		
			Eutectic area	23.5	69.8	26.3	67.6		
37	17.70	71.40	**Sb_2Te_3**	0.5	63.6	-	-		
			(Te)	1.7	97.8	-	-		
			CuTe	47.7	52.3	-	-		
			Eutectic area	23.9	70.9	27.5	66.8		
38	25.00	65.00	**Sb_2Te_3**	6.1	55.8	-	-		
			CuTe	43.1	39.5	-	-		
			Eutectic area	25.4	69.2	25.8	68.5		
39	32.50	50.00	**Sb_2Te_3**	3.5	59.0	-	-	≈514	L + ε-Cu_2Te → Cu_4Te_3 + Sb_2Te_3 (U_5)
			Cu_4Te_3	56.4	41.4	-	-		
			CuTe	-	-	-	-	≈413	L + Cu_4Te_3 → CuTe + Sb_2Te_3 (U_8)
			Eutectic area	28.0	47.9	29.8	50.3		
								526	L + Sb_2Te_3 → γ-(Sb, Te) + ε-Cu_2Te (U_3)
40	30.00	55.00	**Sb_2Te_3**	6.6	58.0	-	-		
			CuTe	48.1	49.8	-	-		
			(Te)	-	-	-	-		

The '≈' symbol denotes that the corresponding value was determined from a single alloy.