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# Journal of Alloys and Compounds



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# Interaction of the components in the Ag-Er-Sn system at 400 °C

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#### ARTICLE INFO

Article history: Received 22 February 2010 Received in revised form 7 April 2010 Accepted 22 April 2010 Available online 15 May 2010

Keywords: Phase diagram Ag–Er–Sn X-ray diffraction Scan electron microprobe

## 1. Introduction

Phase diagram is the "roadmap" for the materials design. Experimental data of the phase equilibria are fundamental for the materials design based on the CALPHAD method [1], and subsequent Phase Field Simulation [1,2]. Moreover, exploration on the phase diagram always accompanied the discovery of new intermetallics, which might be the potential functional materials. However, knowledge of the phase equilibria in some ternary alloys is incomplete and even scarce. As to the RE–Ag–Sn alloys, phase equilibria in the RE (RE=La, Ce, Pr, Nd, Gd, Dy, Yb) –Ag–Sn [3–9] have been reported in the form of isothermal section. Up to now, the phase equilibria in the Ag–Er–Sn system are not yet studied. To extend our knowledge of the RE–Ag–Sn alloys, we aim to determine the phase relationship of the Ag–Er–Sn system in this work.

Massalski [10] assessed the Er–Sn system mainly based on two incomplete phase diagrams established by Love [11] in composition range from 0 to 33.3 at.% Sn and Kulagina et al. [12] from 66.7 to 100 at.% Sn, respectively. According to Massalski [10], five intermetallic compounds formed in this system, i.e.,  $Er_2Sn$ ,  $Er_5Sn_3$ ,  $Er_{11}Sn_{10}$ ,  $ErSn_2$  and  $ErSn_3$ . Palenzona and Manfrinetti [13] later identified the existence of  $Er_2Sn_5$  when reinvestigating the Snrich part of this system. Except  $Er_2Sn$ , recent investigations on the Co–Er–Sn [14] and Cu–(Sm,Er)–Sn [15] ternary systems confirmed the existence of  $Er_5Sn_3$ ,  $Er_{11}Sn_{10}$ ,  $ErSn_2$ ,  $Er_2Sn_5$  and  $ErSn_3$ .

# ABSTRACT

The phase equilibria in the Ag–Er–Sn ternary system at 400 °C were studied over the whole composition range by means of X-ray diffraction and scan electron microscope and energy dispersive X-ray spectroscopy. A new ternary compound with composition of  $Er_{24.6}Ag_{18.9}Sn_{56.5}$ , designed  $\tau$ , and binary phase  $Er_3Sn_7$  had been discovered. The  $Er_3Sn_7$  phase adopts the  $Tb_3Sn_7$  structure type with lattice constants of a = 0.4377 (1) nm, b = 2.5578 (9) nm and c = 0.4333 (2) nm. Other two ternary compounds, i.e., AgErSn<sub>2</sub> and AgErSn, were confirmed, too.

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Three compounds exist in the Ag–Er system: AgEr,  $AgEr_2$  and  $Ag_{51}Er_{14}$  [16]. As regarding to the Ag–Sn binary system, two binary compounds,  $Ag_3Sn$  and  $Ag_4Sn$ , were reported [17].

Two ternary compounds were known for the Ag–Er–Sn system, i.e., AgErSn [18] and AgErSn<sub>2</sub> [19]. Table 1 summarized the crystallographic data of the binary boundary phases and ternary compounds in this system.

#### 2. Experimental procedures

Fifty-five alloy buttons with the weight of 2 g each were prepared by arc-melting the pure elemental Ag (99.9 wt.%), Er (99.9 wt.%) and Sn (99.9 wt.%) under high purity argon atmosphere. To improve the homogeneity, each of the alloys were turned over and remelted for three times. Weight losses for the specimens range from about 1 to 1.5 wt%. No chemical analysis was carried out for the alloys. The ingots were then sealed in evacuated silica capsules, and annealed at 400 °C for 30 days. After completion of annealing, the samples were quenched in water with the tubes not broken.

X-ray diffraction (XRD) was performed with Rikagu-2500 diffractometer with CuK $\alpha$  operating at tube voltage of 40 kV and current of 250 mA. The lattice parameters were calculated by using the WinPLOTR program package [20]. Microstructural examination and composition microanalysis were carried out by using Hitachi 3400N scanning electron microscope (SEM) equipped with EDAX energy dispersive spectrometer (EDS).

### 3. Results and discussion

Table 2 summarizes the experimental results of XRD for the selected alloys. Those severely oxidized alloys are rejected in Table 2. Some off-equilibrium alloys were also collected in Table 2, as they substantiated the existence of some binary or ternary phases. Based on the data available in Table 2, the phase equilibria in Ag–Er–Sn are drawn in Fig. 1. Similar to other M(M=Cu, Ag, Au)–RE–Sn systems, the alloys within or close to the region

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# Table 1

Crystallographic data of already known binary boundary phases and ternary compounds in the Ag–Er–Sn system.

Phases	Space group	Pearson symbol	Prototype	Lattice parameters (nm)			References
				a	b	С	
$ErSn_3^a$ $ErSn_3^b$ $Er_2Sn_5$ $ErSn_2$ $Er_1Sn_{10}$ $Er_5Sn_3$ $AgEr$ $Ag_2Er$ $Ag_2Er$ $Ag_3Sn$ $Ag_4Sn$	Pm3m Amm2 Cmcm I4/mmm P63/mcm Pm3m I4/mmm P6/m Pmmn P6/m Pmmn P63/mmc	CP4 oC16 oC12 tl84 hP16 cP2 tl6 hP68 oP8 hP2	$\begin{array}{c} AuCu_{3}\\ GdSn_{2.75}\\ Y_{2}Sn_{5}\\ ZrSi_{2}\\ Ho_{11}Ge_{10}\\ Mn_{5}Si_{3}\\ CsCl\\ MoSi_{2}\\ Ag_{51}Gd_{14}\\ Cu_{3}Ti\\ Mg\\ \end{array}$	0.4648 (2) 0.4336 0.4305 0.4365 (2) 1.144 0.8799 0.3574 (2) 0.3668 (1) 1.24880 0.47802 (4) 0.29658	0.4367 0.4391 1.6132 (5) 0.5968 (9)	2.1685 1.8892 0.4285 (2) 1.674 0.6442 0.9159 (1) 0.91730 0.51843 (9) 0.47824	[18] [13] [13] [18] [18] [18] [18] [18] [18] [18] [18
AgErSn AgErSn <sub>2</sub>	P63/mmc Pm3m	hP6 cP4	CaIn <sub>2</sub> AuCu <sub>3</sub>	0.4661 (3) 0.45344 (2)		0.7291 (5)	[18] [19]

<sup>a</sup> High temperature phase.
 <sup>b</sup> Low temperature phase.

#### Table 2

Summary of experimental results of XRD for the selected alloys.

	Nominal composition (at.%)		ition(at.%)	Phase identified by XRD	Space group	Structure type	Lattice parameters (nm)	
	Sn	Ag	Er					
1	65	25	10	Er <sub>3</sub> Sn <sub>7</sub> Liquid [(Sn)+Ag <sub>3</sub> Sn]	Cmmm	Tb <sub>3</sub> Sn <sub>7</sub>	a = 0.4377(1), b = 2.5578(9), c = 0.4333(2)	
2 <sup>a</sup>	35	50	15	AgErSn <sub>2</sub>	$Pm\overline{3}m$	AuCu <sub>3</sub>	a = 0.45048(1)	
				Ag <sub>3</sub> Sn	Pos/mmc Pmmn	Cu <sub>3</sub> Ti	a = 0.46438(3), c = 0.72492(7) a = 0.4769(2), b = 0.5952(3), c = 0.5185(3)	
				τ	Structure unknown	Trace		
3	25	60	15	AgErSn	P63/mmc	CaIn <sub>2</sub>	a = 0.46583(1), c = 0.72946(2)	
				Ag <sub>4</sub> Sn	P63/mmc	Mg	a = 0.29689(2), c = 0.47859(7)	
4	10	70	20	AgErSn	P63/mmc	CaIn <sub>2</sub>	a = 0.46645(3), c = 0.72939(6)	
				(Ag)	Fm3m	Cu	a = 0.40883(2)	
				Ag <sub>51</sub> Er <sub>14</sub>	P6/m	$Ag_{51}Gd_{14}$	a = 1.2541(1), c = 0.9244(1)	
5	15	55	30	AgErSn	P63/mmc	CaIn <sub>2</sub>	a = 0.46622(1), c = 0.72845(3)	
				Ag <sub>51</sub> Er <sub>14</sub>	P6/m	$Ag_{51}Gd_{14}$	<i>a</i> = 1.25906(8), <i>c</i> = 0.92222(7)	
6	10	50	40	Er <sub>5</sub> Sn <sub>3</sub>	P63/mcm	$Mn_5Si_3$		
				Ag <sub>2</sub> Er	I4/mmm	MoSi <sub>2</sub>		
7	20	30	50	Er <sub>5</sub> Sn <sub>3</sub>	P63/mcm	Mn <sub>5</sub> Si <sub>3</sub>	a = 0.88086(4), c = 0.64392(3)	
				Ag <sub>2</sub> Er	I4/mmm	MoSi <sub>2</sub>	a = 0.36689(4), c = 0.9158(1)	
				AgEr	Pm3m	CsCl	Trace	
8	20	15	65	Er <sub>5</sub> Sn <sub>3</sub>	P63/mcm	Mn <sub>5</sub> Si <sub>3</sub>	a = 0.88132(2), c = 0.64474(1)	
				AgEr	Pm3m	CsCl	a = 0.35841(2)	
				(Er)	P63/mmc	Mg	a = 0.35707(5), c = 0.55988(3)	
9	10	20	70	Er <sub>5</sub> Sn <sub>3</sub>	P63/mcm	Mn <sub>5</sub> Si <sub>3</sub>	a = 0.87992(3), c = 0.64340(2)	
				AgEr	$Pm\overline{3}m$	CsCl	a = 0.35787(2)	
				(Er)	P63/mmc	Mg	a = 0.35667(3), c = 0.56116(7)	
10	50	15	35	AgErSn	P63/mmc	Caln <sub>2</sub>	a = 0.46624(1), c = 0.72912(2)	
				ErSn <sub>2</sub>	Cmcm	ZrSi <sub>2</sub>	a = 0.43684(2), b = 1.61224(8), c = 0.42853(2)	
				AgErSn <sub>2</sub>	Pm3m	AuCu <sub>3</sub>	a = 0.45156(1)	
11	48	20	32	AgErSn	P63/mmc	Caln <sub>2</sub>	a = 0.46631(1), c = 0.72916(2)	
				ErSn <sub>2</sub>	Cmcm	ZrSi <sub>2</sub>	a = 0.43692(2), b = 1.61277(9), c = 0.42880(2)	
				AgErSn <sub>2</sub>	$Pm\overline{3}m$	AuCu3	a=0.45155(1)	
12	51	20	29	AgErSn	P63/mmc	Caln <sub>2</sub>	a = 0.46607(4), c = 0.7276(1)	
				ErSn <sub>2</sub>	Cmcm	ZrSi <sub>2</sub>	Trace	
				AgErSn <sub>2</sub>	Pm3m	AuCu3	a = 0.45171(9)	
13	55	17	28	AgErSna	$Pm\overline{3}m$	AuCua	a = 0.45297(6)	
	00		20	ErSn <sub>2</sub>	Cmcm	ZrSi2	Trace, not determined	
14	61	10	29	AgerSna	$Pm\overline{3}m$	AuCua	a = 0.45379(1)	
	01	10	23	FrSn <sub>2</sub>	Cmcm	ZrSia	a = 0.43623(2) $b = 1.61152(9)$ $c = 0.42815(2)$	
15 <sup>a</sup>	63	10	27	AgerSna	Pm3m	AuCua	a = 0.45279(2)	
15	05	10	27	FrSna	Cmcm	ZrSi <sub>2</sub>	a = 0.43584(3) $b = 1.6099(1)$ $c = 0.42781(3)$	
				Er <sub>2</sub> Sn <sub>7</sub>	Cmmm	Th <sub>2</sub> Sn <sub>7</sub>	a = 0.43842(4) $b = 2.5414(2)$ $c = 0.43394(4)$	
				(Sn)	I41/amd	Sn	a = 0.58192(2), c = 0.31684(1)	
				Ag <sub>2</sub> Sn	Pmmn	CuaTi	a = 0.4776(2) $b = 0.5974(3)$ $c = 0.5194(2)$	
16 <sup>b</sup>	70	10	20	Er <sub>2</sub> Sn <sub>5</sub>	Pmmn	EraGes	a = 0.4298(2), b = 0.4389(2), c = 1.8867(5)	
10		10	20	Er <sub>2</sub> Sn <sub>7</sub>	Cmmm	$Tb_2 Sn_7$	a = 0.4376(1), b = 2.5534(1), c = 0.4330(1)	
				(Sn)	I41/amd	Sn	a = 0.58303(2), c = 0.31818(1)	
				Ag <sub>3</sub> Sn	Pmmn	Cu <sub>3</sub> Ti	a = 0.4803(3), b = 0.5965(1), c = 0.5190(3)	
17	45	10	45	AgErSn	P63/mmc	CaIn <sub>2</sub>	a = 0.46609(2), c = 0.72931(4)	
	-		-	ErSn <sub>2</sub>	Cmcm	ZrSi <sub>2</sub>	a = 0.43705(4), b = 1.6129(2), c = 0.42885(4)	
				$Er_{10}Sn_{11}?$	I4/mmm	Ho11Ge10		

Table 2(Continued)

Sn         As         Er           18         73         0         27         Er,Sn, Er		Nomir	Nominal composition (at.%)		Phase identified by XRD	Space group	Structure type	Lattice parameters (nm)	
		Sn	Ag	Er					
	18	73	0	27	Er <sub>2</sub> Sn <sub>5</sub>	Pmmn 14. Jamd	Er <sub>2</sub> Ge <sub>5</sub>	a = 0.43007(5), b = 0.43741(5), c = 1.8872(3) a = 0.58257(2), b = 0.21700(1)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	19	70	0	30	$Er_2Sn_5$	Pmmn	Er <sub>2</sub> Ge <sub>5</sub>	a = 0.43001(4), b = 0.43746(4), c = 1.8871(2)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20	0	50	50	ErSn <sub>2</sub> Er <sub>11</sub> Sn <sub>10</sub>	Cmcm I4/mmm	ZrSi <sub>2</sub> Ho <sub>11</sub> Ge <sub>10</sub>		
21       57       57       38       Ag15h; B55h; Ag55h	24		-	20	ErSn <sub>2</sub>	Cmcm	ZrSi <sub>2</sub>		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	21	57	5	38	Agersn <sub>2</sub> ErSn <sub>2</sub>	Рт3т Стст	ZrSi <sub>2</sub>		
23         40         32         28         AgEs7 AgEs	22	30	20	50	Er <sub>5</sub> Sn <sub>3</sub>	P63/mcm	Mn <sub>5</sub> Si <sub>3</sub>	a = 0.8802(5), c = 0.6502(3)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					AgerSn AgeFr ?	P63/mmc I4/mmm	Caln <sub>2</sub> MoSia	a = 0.4668(6), c = 0.7302(8) Trace	
24         40         40         Ags.5n         Pmm         Cu_1Ti $a=0.4732(2), b=0.5952(2), c=0.5178(2)$ 24         40         40         Agt.5n         Pm3m         Act.0u $a=0.45078(1)$ $a=0.45078(1)$ 25         30         45         25         Agt.5n         Pmm         Cu_1Ti $a=0.47946(7), b=0.59178(2), c=0.5198(8), c=0.51973(2), c=0.5198(8), c$	23	40	32	28	AgErSn	P63/mmc	CaIn <sub>2</sub>	<i>a</i> = 0.46631(1), <i>c</i> = 0.72919(2)	
24         40         50         40         70 <th70< th="">         70         70         70&lt;</th70<>					Ag <sub>3</sub> Sn	Pmmn	Cu₃Ti	a = 0.4783(2), b = 0.5959(2), c = 0.5179(2)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	24	40	40	20	AgerSn <sub>2</sub> AgerSn	Pm3m P63/mmc	AuCu <sub>3</sub> CaIn <sub>2</sub>	a = 0.45078(1) a = 0.46656(2), c = 0.72962(2)	
AgESng         April Nm         AuCus         a=0.45164(1)           25         30         45         25         AgESn         Pmmn         Culp:         a=0.453164(1)         a=0.47805(9), b=0.5973(2), c=0.5186(2)           26         10         40         50         AgSn         Pmmn         CujTi         a=0.47805(9), b=0.5973(2), c=0.5186(2)           27 <sup>a</sup> 65         200         15         Er,Snr         MSincm         MpSincm         MpSincm           27 <sup>b</sup> 65         200         15         Er,Snr         Pmmn         CuyTi           7         7         60         20         20         r         Structure unknown           7         7         60         20         20         r         Structure unknown           28 <sup>a</sup> 60         20         20         r         Structure unknown         CuyTi           30 <sup>a</sup> 58         20         Er,Snr         Pmmn         CuyTi         a=0.43758(1), b=2.5540(9), c=0.43308(1)           31 <sup>b</sup> 60         15         20         Er,Snr         Pmmn         CuyTi         a=0.43758(1), b=2.5540(9), c=0.43308(1)           31 <sup>b</sup> 61         15         25         Er,Snr					Ag <sub>3</sub> Sn	Pmmn	Cu <sub>3</sub> Ti	a = 0.47946(7), b = 0.59178(9), c = 0.51509(8)	
25       30       45       25       AggSn       Pos/mmc       Cup: $a = 0.49036(1), e = 0.5973(2), c = 0.5186(2)$ 26       10       40       50       AggSn       Pmm       Cup: $a = 0.49036(1), e = 0.5973(2), c = 0.5186(2)$ 27 <sup>h</sup> 65       20       15       Er.Sn;       Pos/mm       MasSi;         27 <sup>h</sup> 65       20       15       Er.Sn;       Pos/mm       MasSi;         28 <sup>h</sup> 60       20       20       r       Structure unknown       MasSi;         28 <sup>h</sup> 65       15       20       Fr.Sn;       Cmm       Tos, Sn;         29 <sup>h</sup> 65       15       20       Fr.Sn;       Cmm       Tos, Sn;         29 <sup>h</sup> 65       15       20       Fr.Sn;       Cmm       Tos, Sn;         30 <sup>h</sup> 58       20       22       r       Structure unknown       CupTi $a = 0.4813(6), b = 0.594(6), c = 0.513(5);         31h       60       15       25       Er,Sn;       Cmm       Tos, Sn;         32h       51       25       Er,Sn;       Cmm       Tos, Sn;         31h       60       15       25       Er,Sn;       $	25	20	45	25	AgErSn <sub>2</sub>	$Pm\overline{3}m$	AuCu <sub>3</sub>	a = 0.45164(1)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	25	30	45	25	Agersn Ag <sub>2</sub> sn	P63/mmc Pmmn	Caln <sub>2</sub> CuaTi	a = 0.46638(1), c = 0.72932(2) a = 0.47805(9), b = 0.5973(2), c = 0.5186(2)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	26	10	40	50	Ag <sub>2</sub> Er	I4/mmm	MoSi <sub>2</sub>	<i>a</i> 0. 17003(3), <i>b</i> 0.3373(2), <i>c</i> 0.3100(2)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					$Er_5Sn_3$	P63/mcm	Mn <sub>5</sub> Si <sub>3</sub>		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	27 <sup>b</sup>	65	20	15	$Er_3Sn_7$	Cmmm Structure unknown	Tb <sub>3</sub> Sn <sub>7</sub>		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Ag₃Sn	Pmmn	Cu₃Ti		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					(Sn)	I4 <sub>1</sub> /amd	Sn		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	28 <sup>b</sup>	60	20	20	τ Ag-Sp	Structure unknown	Cu-Ti		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					(Sn)	$I4_1/amd$	Sn		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	29 <sup>b</sup>	65	15	20	Er <sub>3</sub> Sn <sub>7</sub>	Cmmm	$Tb_3Sn_7$	a = 0.43758(1), b = 2.5540(9), c = 0.43306(1)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Ag <sub>3</sub> Sn	Pmmn M. Jamd	Cu <sub>3</sub> Ti	a = 0.4813(6), b = 0.5948(5), c = 0.5193(5)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	30 <sup>b</sup>	58	20	22	τ	Structure unknown	511	u = 0.58522(2), c = 0.51810(1)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Ag <sub>3</sub> Sn	Pmmn	Cu <sub>3</sub> Ti		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	31b	60	15	25	(Sn) Fr-Sn-	I4 <sub>1</sub> /amd	Sn Th-Sn-		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	51	00	15	25	τ	Structure unknown	1035117		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Ag <sub>3</sub> Sn	Pmmn	Cu₃Ti		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3.2p	52	28	20	(Sn) T	I4 <sub>1</sub> /amd	Sn		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	52	52	20	20	ر Ag₃Sn	Pmmn	Cu <sub>3</sub> Ti		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					(Sn)	I4 <sub>1</sub> /amd	Sn		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	33	14	62	24	AgErSn	P63/mmc	Caln <sub>2</sub>	a = 0.46637(3), c = 0.72800(6)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					$(Ag_{51}Er_{14})$	P6/m	$Ag_{51}Gd_{14}$	a = 1.2578(1), c = 0.9221(1)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	34	23	46	31	AgErSn	P63/mmc	Caln <sub>2</sub>	a = 0.46604(2), c = 0.72797(4)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					(Ag)	Fm3m	Cu	a = 0.4020(2)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	35	52	26	22	$\pi Rg_{51}Er_{14}$	Po/m Structure unknown	Ag <sub>51</sub> Gd <sub>14</sub>	<i>u</i> = 1.2564(3), <i>c</i> = 0.9235(3)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Ag <sub>3</sub> Sn	Pmmn	Cu <sub>3</sub> Ti		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	36	65	0	35	ErSn <sub>2</sub>	Cmcm	ZrSi <sub>2</sub>	a = 0.43579(6), b = 1.6108(2), c = 0.4275(6)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	37 <sup>b</sup>	55	20	25	(Sn) τ	141/ama Structure unknown	Sn	a = 0.58308(3), c = 0.31817(1)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					Ag₃Sn	Pmmn	Cu <sub>3</sub> Ti		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 oh	55	22	22	(Sn)	I4 <sub>1</sub> /amd	Sn		
39 <sup>b</sup> 55 18 27 $ au$ (Sn) 141/amd Sn Structure unknown Ag <sub>3</sub> Sn Pmmn Cu <sub>3</sub> Ti	38°	22	22	23	Ag <sub>3</sub> Sn	Pmmn	Cu₃Ti		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					(Sn)	I4 <sub>1</sub> /amd	Sn		
Ag <sub>3</sub> Sn Pmmn Cu <sub>3</sub> Ti	39 <sup>b</sup>	55	18	27	T Am Cm	Structure unknown	Cir Ti		
$(Sn)$ $I_{4_1}/amd$ $Sn$					Ag <sub>3</sub> Sn (Sn)	Pmmn I41/amd	Sn		
40 50 25 25 AgErSn <sub>2</sub> $Pm\overline{3}m$ AuCu <sub>3</sub> $a = 0.45095(7)$	40	50	25	25	AgErSn <sub>2</sub>	Pm3m	AuCu <sub>3</sub>	<i>a</i> = 0.45095(7)	

<sup>a</sup> The alloys are off-equilibrium.

<sup>b</sup> Ag<sub>3</sub>Sn and (Sn) in these alloys resulted from the solidification of liquid during the quench.

of  $\text{Er}_5\text{Sn}_3$  to  $\text{Er}_{11}\text{Sn}_{10}$  were found sensitive to moisture and oxygen and were readily discarded. For this reason, we could not observe  $\text{Er}_{11}\text{Sn}_{10}$  in the ternary alloys. Thus, the  $\text{Er}_{11}\text{Sn}_{10}$  related tie-triangles are connected with dot line. Single AgErSn<sub>2</sub> phase was obtained in alloy 40 (Ag<sub>25</sub>Er<sub>25</sub>Sn<sub>50</sub>), and its lattice parameter was calculated to be *a* = 0.45095 (7) nm. For AgErSn<sub>2</sub>, its lattice constant was found significant change in alloys 11–14 with the variation of the alloys' composition. The fact implies that there is a small homogeneity for this compound.  $Ag_{51}Er_{14}$  and liquid should occupy a certain area considering the adjacent phase relationships. However, no the effort was made to measure the phase boundaries of  $AgErSn_2$  as well as  $Ag_{51}Er_{14}$  and liquid. Thus, the boundaries of these phases were drawn tentatively in Fig. 1. To support the proposed tie triangles, Figs. 2–5 present XRD results of several equilibrated alloys.

In the present work, a new ternary compound, designed  $\tau$ , was found and identified. Fig. 6 presents the XRD results of alloys 28



Fig. 1. Phase equilibria of the Ag–Er–Sn ternary system at 400  $^\circ$ C. The boundaries of AgErSn\_2 and liquid phase and Ag<sub>51</sub>Er<sub>14</sub> are tentative.



Fig. 2. XRD result of alloy 4 annealed at 400  $^\circ$ C for 30 days, showing the co-existence of AgErSn and (Ag) and Ag51Er14.

 $(Ag_{20}Er_{20}Sn_{60})$ , 30  $(Ag_{20}Er_{22}Sn_{58})$  and 32  $(Ag_{28}Er_{20}Sn_{52})$ , where the intense peaks labeled in full circle were identified as  $\tau$ . The peak positions in two-theta attributed to this new ternary compound are listed as follows:  $34.20^{\circ}$ ,  $36.45^{\circ}$ ,  $41.26^{\circ}$ ,  $56.27^{\circ}$ ,  $59.83^{\circ}$ ,  $64.28^{\circ}$ , 70.80° and 72.17°. However, except (Sn) and Ag<sub>3</sub>Sn, there are many



Fig. 3. XRD result of alloy 11 annealed at 400  $^\circ C$  for 30 days, showing the co-existence of AgErSn\_2 and AgErSn and ErSn\_2.



Fig. 4. XRD result of alloy 23 annealed at 400 °C for 30 days, showing the coexistence of AgErSn<sub>2</sub> and AgErSn and Ag<sub>3</sub>Sn.



Fig. 5. XRD result of alloy 7 annealed at 400  $^\circ$ C for 30 days, showing the co-existence of Ag\_2Er and Er\_5Sn\_3.

unidentified weak peaks in Fig. 6. To clarify the composition of this new ternary compound, alloy 32 ( $Ag_{28}Er_{20}Sn_{52}$ ) was subjected to SEM/EDS examination. Matrix  $\tau$  phase and  $Ag_3Sn$  and (Sn) were observed in this alloy. The composition of  $\tau$  was measured to be of 24.6 at.% Ag, 18.9 at.% Er and 56.5 at.% Sn, while that of Ag\_3Sn was 73.6 at.% Ag, 1.1 at.% Er and 25.3 at.% Sn. In order to synthesize this compound, several other alloys, such as alloys 37 ( $Ag_{20}Er_{25}Sn_{55}$ ), 38 ( $Ag_{20}Er_{27}Sn_{55}$ ) and 39 ( $Ag_{18}Er_{27}Sn_{55}$ ), were melted and annealed



**Fig. 6.** The XRD results of alloys 28 ( $Ag_{20}Er_{20}Sn_{60}$ ), 30 ( $Ag_{20}Er_{22}Sn_{58}$ ) and 32 ( $Ag_{28}Er_{20}Sn_{52}$ ). Except those of (Sn) and  $Ag_3Sn$ , peaks labeled in full circle were identified as to the new ternary compound  $\tau$ .



Fig. 7. XRD patterns of alloy 37  $(Ag_{20}Er_{25}Sn_{55})$  annealed at 400 and 500  $^\circ\text{C},$  respectively.

at 400 °C for 7 days. Due to the segregation of (Sn), we failed to obtain single ternary compound  $\tau$ .

The new ternary compound  $\tau$  was found to disappear when the alloy was annealed at 500 °C for 7 days followed by water quenching. Fig. 7 compares the XRD results of alloy 37 (Ag<sub>20</sub>Er<sub>25</sub>Sn<sub>55</sub>) heated at 400 and 500 °C, respectively. As shown in Fig. 7, new ternary phase  $\tau$  and (Sn) and Ag<sub>3</sub>Sn as well as trace amount of Er<sub>2</sub>O<sub>3</sub> co-exist in the alloy heated at 400 °C. When temperature rises to 500 °C, Ag<sub>3</sub>Sn and those peaks attributed to the new ternary compound as well as the unknown weak peaks vanished with the formation of AgErSn<sub>2</sub>. This fact suggested that those unknown weak peaks mentioned above might belong to  $\tau$  phase, as shown in Fig. 7.

X-ray patterns similar to Tb<sub>3</sub>Sn<sub>7</sub> were observed in several ternary alloys, which implied that Er<sub>3</sub>Sn<sub>7</sub> might form in the Er–Sn side. Fig. 8 presents the XRD results of alloys 1 (Ag<sub>25</sub>Er<sub>10</sub>Sn<sub>65</sub>) and 16 (Ag<sub>10</sub>Er<sub>20</sub>Sn<sub>70</sub>), where the peaks labeled in full circle are attributed to Er<sub>3</sub>Sn<sub>7</sub>. By assuming Er<sub>3</sub>Sn<sub>7</sub> isostructural to Tb<sub>3</sub>Sn<sub>7</sub>, fair agreement in the calculated and observed peak intensities was obtained. Therefore, Er<sub>3</sub>Sn<sub>7</sub> was believed to exist in the Er–Sn system. This conclusion is in contradiction to the results of Palenzona and Manfrinetti [13], in which RE<sub>3</sub>Sn<sub>7</sub> type phases were excluded in (Er, Ho, Tm, Lu)–Sn systems but included in (Gd, Tb, Dy, Y)–Sn systems. The cell parameters of Er<sub>3</sub>Sn<sub>7</sub> are calculated to be a = 0.4377 (1) nm, b = 2.5578 (9) nm and c = 0.4333 (2) nm in alloy 1 (Ag<sub>25</sub>Er<sub>10</sub>Sn<sub>65</sub>). As shown in Fig. 8, alloy 16 (Ag<sub>10</sub>Er<sub>20</sub>Sn<sub>70</sub>)



**Fig. 8.** The XRD results of alloys 16 (Ag<sub>10</sub>Er<sub>20</sub>Sn<sub>70</sub>) and 1 (Ag<sub>25</sub>Er<sub>10</sub>Sn<sub>65</sub>) annealed at 400 °C for 30 days followed by water quenching. Alloy 16 (Ag<sub>10</sub>Er<sub>20</sub>Sn<sub>70</sub>) is composed of Er<sub>2</sub>Sn<sub>5</sub>, Er<sub>3</sub>Sn<sub>7</sub>, Ag<sub>3</sub>Sn and (Sn), while alloy 1 (Ag<sub>25</sub>Er<sub>10</sub>Sn<sub>65</sub>) consists of Er<sub>3</sub>Sn<sub>7</sub>, Ag<sub>3</sub>Sn and (Sn). The latter two phases are the liquid products during the solidification.



Fig. 9. XRD results of alloy 18 ( $Er_{27}Sn_{73}$ ) annealed at (1) 700 °C for 30 days and (2) further annealed at 400 °C for 7 days.

is composed of  $Er_2Sn_5$ ,  $Er_3Sn_7$ ,  $Ag_3Sn$  and (Sn), while alloy 1 ( $Ag_{25}Er_{10}Sn_{65}$ ) consists of  $Er_3Sn_7$ ,  $Ag_3Sn$  and (Sn). The latter two phases are the liquid products during the solidification.

Alloys 18 (Er<sub>27</sub>Sn<sub>73</sub>) and 19 (Er<sub>30</sub>Sn<sub>70</sub>) were prepared to verify the existence of Er<sub>2</sub>Sn<sub>5</sub>. Er<sub>3</sub>Sn<sub>7</sub> was thought to form through peritectic reaction at a temperature higher than that of Er<sub>2</sub>Sn<sub>5</sub>. Alloy 19 was expected to consist of single  $Er_3Sn_7$  or  $(Er_3Sn_7 + Er_2Sn_5)$ , if the practical composition of alloy only slightly deviated from the nominal composition. Thus, a higher annealing temperature 700 °C was arbitrarily chosen for these two alloys for the first time. Apart from Er<sub>2</sub>Sn<sub>5</sub> and Sn, XRD detected additional trace amount of ErSn<sub>2</sub> for alloy 19 (Er<sub>30</sub>Sn<sub>70</sub>) and orthorhombic ErSn<sub>3</sub> for alloy 18 (Er<sub>27</sub>Sn<sub>73</sub>), after annealed at 700 °C for 30 days followed by air-cooling. When both alloys were re-heated at 400 °C for 7 days and followed by water quenching, alloy 19 ( $Er_{30}Sn_{70}$ ) was observed to consist of Er<sub>2</sub>Sn<sub>5</sub> and ErSn<sub>2</sub> with (Sn) almost vanished, while alloy 18 (Er<sub>27</sub>Sn<sub>73</sub>) consisted of Er<sub>2</sub>Sn<sub>5</sub> and (Sn) with ErSn<sub>3</sub> thoroughly disappeared. Fig. 9 presents the XRD results of alloy 18 (Er<sub>27</sub>Sn<sub>73</sub>). Er<sub>2</sub>Sn<sub>5</sub> was reported to adopt the Y<sub>2</sub>Sn<sub>5</sub> crystal structure [13]. However, we could not find the crystal structural data of Y<sub>2</sub>Sn<sub>5</sub> in the public literature. Recently, Venturini et al. determined the crystal structure of Er<sub>2</sub>Ge<sub>5</sub> (space group, Pmmn) [21]. We thought that Er<sub>2</sub>Sn<sub>5</sub> might be isostructural to Er<sub>2</sub>Ge<sub>5</sub>. Thus, substituting Sn into the positions of Ge, the XRD pattern of Er<sub>2</sub>Sn<sub>5</sub> was calculated by using the Powdercell program [22]. Comparing the calculated patterns, Er<sub>2</sub>Sn<sub>5</sub> was found to show strong preferred orientation in all the investigated alloys. As shown in Fig. 9, the (007) peak was observed to be the most intense while the theoretical strongest peak (113) to be the third intense.

Palenzona and Manfrinetti [13] indicated that the RSn<sub>2</sub> compounds showed very high stability, and could not be destroyed by annealing treatment unless remelting the alloy. This suggestion might be right for the binary alloys. However, for the ternary alloys, the suggestion might be questionable. In the present work,  $ErSn_2$  and cubic-AgErSn<sub>2</sub> as well as (Sn) and Ag<sub>3</sub>Sn were observed in the as-cast alloy 28 (Ag<sub>20</sub>Er<sub>20</sub>Sn<sub>60</sub>). When this alloy is subjected to annealing at 400 °C for 20 days,  $ErSn_2$  and cubic-AgErSn<sub>2</sub> vanished and the new ternary compound  $\tau$  formed.

#### 4. Conclusions

Phase equilibria of the Ag–Er–Sn ternary system were determined. Two new compounds, i.e.,  $Er_3Sn_7$  and  $\tau$ , were identified for the first time. The  $Er_3Sn_7$  phase crystallizes in Tb<sub>3</sub>Sn<sub>7</sub> structure type with cell parameters of a=0.4377 (1)nm, b=2.5578 (9)nm and c = 0.4333 (2) nm. The compositions of  $\tau$  were measured to be of 24.6 at.% Ag, 18.9 at.% Er and 56.5 at.% Sn.

#### Acknowledgements

Financial supports from the Guangxi Science Foundation (Contract Nos. 0448022, 0542009 and 0640040), and Guangxi Large Scale Apparatus Corporation Office are greatly appreciated.

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