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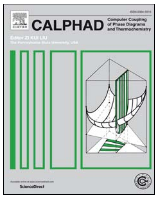

Experimental investigation of phase relations in Bi-Te-RE (Yb, La, Ce) ternary systems

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ABSTRACT

Rare earth (RE) elements especially Yb, La and Ce have been frequently doped to Bi-Te alloys to improve thermoelectric performance. Three isothermal sections: Bi-Te-Yb at 573 K, Bi-Te-La and Bi-Te-Ce at 673 K were partly established by means of electron probe micro-analysis (EPMA) and powder X-ray diffractometry (XRD). The determined maximum solubilities of RE elements in Bi-Te alloys are very small and that of Yb reached the maximum about 0.3 at% at 573 K. Both $LaTe_2$ and $CeTe_2$ can dissolve a large amount of Bi, about 10 and 13 at% at 673 K, respectively. No ternary compound has been confirmed.

1. Introduction

Thermoelectric (TE) materials are regarded as ideal tools to deal with the environment problems that our world are facing today including energy shortage and ozone layer degradation owing to the capability of thermoelectric power generation and all-solid-state refrigeration [1]. The chalcogenide Bi_2Te_3-related materials are the most prominent and promising room-temperature TE material. However, the conversion efficiency of these materials is insufficient for widespread application. The inherent efficiency of TE material is evaluated by a dimensionless figure of merit ZT ($\alpha^2\sigma T/\kappa$), which shows that efficient thermoelectric material must have a large Seebeck coefficient α, a high electrical conductivity σ as well as a low thermal conductivity κ. Such characteristics are frequently reported in rare earth (RE-)doped semiconductors. Doping with rare-earth atoms, like Ce or Yb, can form resonance electron states near the Fermi level thus modify the carrier concentration and enhance phonons scattering [2–7].

The Ames researchers found that adding just 1at% of the rare-earth elements cerium or ytterbium to a TAGS material ($Ag_{6.5}2Sb_{6.5}2Ge_{36.96}Te_{50.00}$), the figure of merit will increase by 25%, because rare-earth atoms are incorporated into the lattice where they produce large local lattice distortions [7]. It can be deduced that the amount of doped RE atoms which can incorporated into the lattice of matrix, namely solid solubility, is of great importance to design thermoelectric materials [8]. Early attempts also focus on the reported ternary compounds. For example, Guloy et al. [9] found that the lattice thermal conductivity of $YbSb_2Te_4$ is as low as that of glass. The calculation of Singh and Schwingenschlögl [10] turns out $LaBiTe_3$ merges characteristics that are beneficial for thermoelectric devices. The information of both solid solubility and ternary compounds can be always clearly illustrated in the phase diagram [11]. Besides, thermoelectric properties of material are closely related with the crystal structure, thermodynamic stability and phase transformation temperature, which can be easily obtained from the phase diagram and the relevant thermodynamic database [12]. However, there are rare reported investigations about phase relations of lanthanide doped Bi_2Te_3 or any systems consisted of congeners elements. So, to investigate a series of phase diagrams of Bi-Te-RE systems is imperative for the design of Bi-Te based TE materials.

2. Literature review

2.1. The Bi-Te system

The Bi-Te system has been re-investigated both experimentally and thermodynamically by our group recently [13]. It is confirmed that besides Bi_2Te_3, there is a β-phase with a large composition range at low temperature, other than several divided intermediate compounds as reported before. The calculated phase diagram which consists well with the experimental one is shown in Fig. 1.

2.2. The Bi-Te-Yb system

The other sub-systems of Bi-Te-Yb, i.e. Bi-Yb and Te-Yb have also been assessed in recent years [14,15]. Thermodynamic modeling of Te-Yb system was attempted by Ghamri et al. [14] using a sub-regular solution model. Later, Wang et al. [15] calculate this system using associate model for liquid phase description and also assessed Bi-Yb

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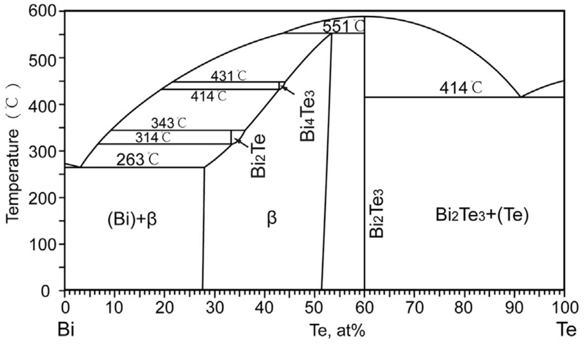

Fig. 1. Calculated Bi-Te phase diagram [13].

Table 1
Crystallographic data of reported intermetallics of Bi-Te-Yb/ La/ Ce systems.

Phase	Protype	Pearson symbol	Space group	Lattice parameters			Refs.
				a(Å)	b(Å)	c(Å)	
Bi_2Te_3	Bi_2Te_3	hR5	R-3m	4.388	4.388	30.488	[13]
Bi_2Te	Bi_2Pb	hP9	P-3m1	4.49	4.49	18.09	[13]
Bi_4Te_3	Bi_4Se_3	hR7	R-3m	4.451	4.451	41.89	[13]
β	*	*	*	*	*	*	[13]
Yb							
YbTe	NaCl	cF8	Fm3m	6.348	6.348	6.348	[14]
Yb_2Bi	*	*	*	*	*	*	[15]
Yb_5Bi_3	Mn_5Si_3	hP16	P63/mcm	9.165	9.165	6.983	[15]
Yb_4Bi_3	Th_3P_4	cI28	I43d	9.554	9.554	9.554	[15]
$Yb_{11}Bi_{10}$	*	*	*	*	*	*	[15]
$YbBi_2$	$ZrSi_2$	oS12	Cmcm	4.642	16.682	4.401	[15]
Yb_4Bi_2Te	Th_3P_4	cI28	I-43d	9.571	9.571	8.289	[17]
$YbBi_4Te_7$	Th_3P_4	cI28	I-43d	10.62	10.62	9.197	[18]
$YbBi_2Te_4$	Th_3P_4	cI28	I-43d	10.48	10.48	9.076	[18]
La							
$LaBi_2$	$LaSb_2$	oC12	I4/mmm	4.564	17.51	4.564	[20]
LaBi	NaCl	cF8	Fm-3m	6.658	6.658	6.658	[20]
La_4Bi_3	Th_3P_4	cI28	I-43d	9.790	9.790	9.790	[20]
La_5Bi_3	Mn_5Si_3	hP16	P63/mcm	9.659	9.659	6.697	[20]
La_2Bi	$LaSb_2$	tI12	I4/mmm	4.737	4.737	18.340	[20]
LaTe	NaCl	cF8	Fm-3m	6.420	6.420	6.420	[27]
La_2Te_3	Th_3P_4	cI28	I-43d	9.619	9.619	9.619	[27]
$La_{2.67}Te_4$	*	*	I-43d	*	*	*	[27]
La_4Te_7	La_4Te_7	tP22	P4/mbm	9.011	9.011	9.172	[26]
$LaTe_2$	Cu_2Sb	tP6	P4/nmm	4.56	4.56	9.12	[27]
$LaTe_3$	$NdTe_3$	tp16	P42/n	4.402	4.402	25.881	[27]
$LaBiTe_3$	Bi_2Te_2S	R-3m	*	4.39	4.39	30.20	[31]
LaBiTe	*	oP*	P212121	10.48	10.48	9.07	[31]
Ce							
$CeBi_2$	*	aP*	*	*	*	*	[33]
CeBi	NaCl	cF8	Fm-3m	6.5	6.5	6.5	[33]
Ce_4Bi_3	Th_3P_4	cI28	I-43d	*	*	*	[33]
Ce_5Bi_3	Mn_5Si_3	hP16	$P6_3$/mcm	*	*	*	[33]
Ce_2Bi	La_2Sb	tI12	I4/mmm	*	*	*	[33]
CeTe	NaCl	cF8	Fm-3m	6.359	6.359	6.359	[34]
Ce_3Te_4	Th_3P_4	cI28	I-43d	9.540	9.540	9.540	[34]
Ce_4Te_7	*	*	*	8.988	8.988	9.167	[34]
$CeTe_2$	Cu_2Sb	tP6	P4/nmm	4.490	4.490	9.100	[34]
Ce_2Te_3	Th_3P_4	cI26.65 cI26.65	I-43d	9.539	9.539	9.539	[34]
$CeTe_3$	$NdTe_3$	oC16	Cmcm	6.361	6.361	6.361	[34]
$CeBiTe_3$	*	h**	*	4.19	4.19	31.6	[35]

Notes:* Information of this part is not clear.

system employing both sub-regular solution model and associate model. Both the optimization results conducted using associate models agree better with experimental data. Five intermetallic compounds, Yb_2Bi, Yb_5Bi_3, Yb_4Bi_3, $Yb_{11}Bi_{10}$ and $YbBi_2$ were included in Bi-Yb binary system, although the crystal structure of $Yb_{11}Bi_{10}$ or Yb_2Bi is still unclear and their PDF card cannot be found. The assessed Te-Yb binary phase diagram contains only one intermediate phase, YbTe. However, the existence of other two intermediate phases: Te_2Yb and Te_3Yb_2 which found before by Slovyanskikh et al. [16] in the samples annealed at 1100 K have not be challenged or investigated in any other literature.

In 1979, Hulliger [17] reported Yb_4Bi_2Te as well as its atomic occupation and crystal structure. Later, two ternary compounds: $YbBi_4Te_7$ and $YbBi_2Te_4$ were reported by Aliev et al. [18]. However, neither experimental data nor other evidence can be found to confirm these three compounds. A quasi-binary section $YbTe$–Bi_2Te_3 was studied recently and the existence of $YbBi_4Te_7$ or $YbBi_2Te_4$ were denied [19]. Furthermore, no isothermal section or vertical section has been reported. The reported crystallographic data of intermetallics in the Bi-Te-Yb system were listed in Table 1.

2.3. The Bi-Te-La system

The sub-system Bi-La has been thermodynamically modeled by Tang et al. [20], using both substitutional solution model (solid line) and associate model (dash line) as shown in Fig. 2(a). The calculation results agree well with most reported experimental data including phase relations determined by Nomura et al. [21] and thermodynamic properties reported in literature [22,23]. The formation temperatures of La_4Bi_3 and LaBi reported in Ref. [21] are 1670 ± 30°C and 1615 ± 15°C, respectively. When using the substitutional model (solid line), these two reaction temperatures were adjusted to ensure right reaction type, but right formation temperature. Whereas using the associate model (dash line), both the calculated temperatures and reaction types for these two reactions always agree with the measured data. There are total five intermediate compounds in the Bi-La phase diagram, i.e. La_2Bi, La_5Bi_3, La_4Bi_3, LaBi, $LaBi_2$.

The reported phase relations of La-Te system are quite old. In the phase diagram established by Eliseev et al. [24], La_4Te_7 is a separated phase, whereas it was included into the homogeneous composition of $LaTe_2$ by Ramsey et al. [25]. The X-ray diffraction spectrum of La_4Te_7 and $LaTe_2$ are quite similar in line distribution and intensity; only several $LaTe_2$ lines are split in the La_4Te_7 photograph and shifted towards larger angles. The line splitting is a result of the lower crystal lattice symmetry [26]. Based on previous findings, Okamoto [27] redrawn the phase diagram as shown in Fig. 2(b). The other solution region $La_{2.67}Te_4$ was later denoted as La_3Te_4, more frequently, La_2Te_3. Besides, there are two stoichiometric phases $LaTe_3$ and LaTe.

The group of Sadygov reported several vertical sections of Bi-Te-La system subsequently: Bi_2Te_3-La_3Te_4 [28], Bi_2Te_3-LaTe [29] and Bi-LaTe, La_4Bi_3-LaTe, La_4Bi_3-Bi_2Te_3, Bi_2Te_3-La [30]. A projection of the ternary liquidus surface was also constructed by them. However, no experimental evidence was provided in their papers. The absence of Te-rich La-Te binary compounds in all these vertical sections encouraged us to focus on phase relations of this corner. Additionally, two ternary compounds: $LaBiTe_3$ and LaBiTe have been reported in this system [31].

2.4. The Bi-Te-Ce system

By evaluating reported experimental information, phase diagram of Bi-Ce system was assembled by Gschneidner and Calderwood [32] then thermodynamically optimized by Juan Li et al. [33]. As illustrated in Fig. 3(a), all intermediate compounds of this system are identical with those of Bi-La system. Comparing the binary phase diagram of Te-Ce system evaluated by Okamoto (in Fig. 3(b)) [34] and the projection of liquidus surface of Ce–Bi–Te ternary system conducted by Mamedova et al. [35] with those of Bi-Te-La summarized above, it can be indicated that the phase relations of Bi-Te-Ce system resemble those of Bi-Te-La. Therefore, it would be rational to investigate these two systems together. Crystallographic data of reported intermetallics of Bi-Te-Ce system are also listed in Table 1.