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Phase diagram of ternary Cu-Ga-Te system and thermoelectric properties of chalcopyrite $CuGaTe_2$ materials

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ABSTRACT

Among all types of thermoelectric materials, chalcopyrite $CuGaTe_2$ has been viewed as a promising candidate for use of thermoelectric generator due to its high figure-of-merit (*zT*) at the high temperatures. Herein the 923 K isothermal section of ternary Cu-Ga-Te system is determined, using various thermally-equilibrated Cu-Ga-Te alloys, and ternary $CuGaTe_2$ phase is stabilized within the compositional region of 48.0–53.0 at%Te and 25.0 at%-30.0 at%Cu. Moreover, the solubility of Cu in binary Ga_2Te_3 and Ga_3Te_4 compounds at 923 K is negligible, while that in GaTe phase reaches 7.9 at%Cu. The as-determined isothermal section, depicting the phase stability regime of $CuGaTe_2$, provides options for precisely locating the compositions of $CuGaTe_2$-based materials that lead to promising and reproducible thermoelectric properties. A *zT* peak of 0.6 has been achieved in the Bridgman-grown $Cu_{25}Ga_{26}Te_{49}$ alloy at 750 K, which is nearly *eight* times higher than the neighboring $Cu_{28}Ga_{25}Te_{47}$ alloy, presumably due to the fact that the $Cu_{25}Ga_{26}Te_{49}$ alloy, which exhibits high phase purity of $CuGaTe_2$, has lower lattice thermal conductivity (κ_L~1.3 (W/mK) and higher power factor (*PF*~11.2 (μW/mK^2)), comparing with that of $Cu_{28}Ga_{25}Te_{47}$ alloy (κ_L~1.8 (W/mK) and *PF*~1.9 (μW/mK^2)), which locates in a three-phased $CuGaTe_2$+Cu_2Te + Cu_9Ga_4 region, with only a slight deviation in the starting composition.

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1. Introduction

Driven by the growing energy demands and globally environmental issues, it is essential to develop clean, sustainable and high-efficiency energy resources, in the hope to reduce the dependence on the fossil fuel. Given that more than 60% of precious energy is not properly used and mostly being discharged as waste heat, high-efficiency thermoelectric materials and modules, which can convert great amount of waste heat into precious electricity via Seebeck effect [1–3], have attracted actively interests in the field of waste heat recovery [4–6].

The thermal-to-electricity conversion efficiency for a certain thermoelectric material is related to a dimensionless figure-of-merit ($zT=(S^2/\kappa\rho)T$), where *S* is the Seebeck coefficient, κ is the thermal conductivity, ρ is the electrical resistivity and *T* is the absolute temperature. Provided that the thermoelectric materials exhibit *zT* values greater than 1.5, the resultant device efficiency is likely to reach ~15% [5,7], which makes the thermoelectric technology possible as a cost-effective solution to the energy issues and is competitive with other types of sustainable energy.

Chalcopyrite I-III-VI_2 materials that belong to the space group $I\bar{4}2d$ have long been considered as prospective candidates in various applications, such as photovoltaic and optoelectronic devices, thin-film solar cell, etc. [8–13]. Recent progress in chalcopyrite materials has extended toward the field of thermoelectric generators [7,14–25], leading to the breakthroughs in *zT*s at temperature higher than 700 K. In particular, the hot-pressed *p*-type $CuGaTe_2$ [7], with a band gap of approximately 1.2eV, achieves a *zT* peak of 1.4 at 950 K, resulting from the high Seebeck coefficient (S > 200 (μV/K)), low electrical resistivity (ρ < 5 (mΩcm)) and moderate thermal conductivity (κ~0.9 W/mK). Stoichiometry of the metal elements in chalcopyrite materials, such as Cu in $Cu_{1-x}GaTe_2$ [20] and $Cu_{1-x}InTe_2$ [21] or Ag in $Ag_{1-x}GaTe_2$ [22], etc., is found to have a significant impact upon the resultant thermoelectric properties, presumably due to the fact that adjusting the concentrations of metal elements and vacancies leads to the optimization of carrier concentration (*n*), which directly affect materials' electrical and thermal transport properties (e.g., ρ and *S*). Introducing dopants in chalcopyrite materials also serves as an effective approach in enhancing the *zT*s, mainly as a result of lowering the lattice thermal conductivity (κ_L); examples can be found in Ag-doped $CuAg_xGa_{1-}$

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$_xTe_2$ [23], Gd-doped $CuGa_{1-x}Gd_xTe_2$ [24], Sb-doped $Cu_{1-x}GaSb_xTe_2$ [25], etc., yielding zT peak values of 0.31 at 590 K [23], 0.75 at 737 K [24] and 1.07 at 721 K [25], respectively.

Despite $CuGaTe_2$ shows advances on the field of thermoelectric generator, systematic investigations upon the material are still insufficient, especially in the relations between the phase stability, microstructures and thermoelectric properties. Herein, various ternary Cu-Ga-Te alloys were either thermally-equilibrated at 923 K, to clarify the phase relations and phase stability of ternary $CuGaTe_2$ phase, or grown using the Bridgman method [26], to understand the microstructural features and the formation of precipitates. Attempts to unravel the cause of high-zTs of $CuGaTe_2$ alloys and to locate the possible compositional regions of $CuGaTe_2$-based materials, which exhibit promising and reproducible thermoelectric properties, might be achieved using the combinatorial information of the phase diagram and metallographic observations provided in this study.

2. Experimental procedures

2.1. Synthesis

Pure elements of Cu (99.5%, Alfa Aesar, U.S.A.), Ga (99.999%, Alfa Aesar, U.S.A.) and Te (99.99%, Alfa Aesar, U.S.A.) were weighed according to pre-determined compositions as listed in Table 1 and encapsulated in 7 mm × 9 mm quartz tubes under vacuum. The total amount of each alloy was chosen to be 1 g. The ampoules were placed in a 1273 K furnace for 12 h, followed by water quenching to suppress the grain growth of solidification phases and to maintain the fine-grained microstructure, which ensured the homogenous composition throughout the as-casted alloy. However, for samples with melting points higher than 1273 K (i.e., the Cu-rich samples), arc-melting process under Argon environment was necessary to ensure that the constituent elements were mixed homogeneously without oxidation at high temperatures. Nevertheless, due to the large difference in melting points between Cu (*m.p.* = 1358 K) and Ga (*m.p.* = 303 K) elements and the high vapor pressure of Te element (vapor pressure = 100 kPa at 1266 K), the elements Ga and Te were mixed first in a 973 K furnace under vacuum while the Cu element was added subsequently using arc-melting, to reduce the possible mass loss to less than 5%. After homogenization, the sample ampoules were subjected to annealing process at 923 K for 720 h, followed by water-quenching process again.

Selective ternary Cu-Ga-Te alloys were synthesized using the unidirectional solidification in a Bridgman furnace, and the details of Bridgman method had been reported previously [26,27]. Five grams of homogenized sample ingot with predetermined compositions was loaded in a 7 mm × 9 mm quartz tube, sealed under vacuum and placed in a Bridgman furnace equipped with three different heating zones, which allow to create a large temperature gradient of 50 (K/mm) along the axial direction. At very beginning of unidirectional solidification, the ampoule was placed in the high-temperature zone where the temperature was set to be higher than the melting points of the selective alloys (~1123 K) for 30 min, and then the ampoule moved downward gradually, at the rate of 5 (mm/hr), from the high-temperature zone (~1123 K) to the low-temperature zone (~room temperature). Consequently, the polycrystalline Bridgman-grown alloys with composition nearing the stoichiometric $CuGaTe_2$ phase, labeled with alloy #A ($Cu_{25}Ga_{25}Te_{50}$), alloy #B ($Cu_{29}Ga_{22}Te_{49}$), alloy #C ($Cu_{25}Ga_{26}Te_{49}$), alloy #D ($Cu_{27}Ga_{25}Te_{48}$), alloy #E ($Cu_{30}Ga_{22}Te_{48}$) and alloy #F ($Cu_{28}Ga_{25}Te_{47}$) for the following discussion, were subjected to further thermoelectric properties measurements.

Table 1
Nominal composition of Cu-Ga-Te ternary alloys equilibrated at 923 K together with their equilibrium phases.

No. of alloy	Nominal composition (at%)			Equilibrium phase	Composition of equilibrium phase (at%)		
	Cu	Ga	Te		Cu	Ga	Te
1	20.0	10.0	70.0	$CuGaTe_2$	25.2	21.4	53.4
				Liquid	15.6	3.0	81.4
2	15.0	25.0	60.0	$CuGaTe_2$	25.0	23.5	51.5
				Liquid	2.2	10.2	87.6
3	25.0	20.0	55.0	$CuGaTe_2$	25.9	23.9	50.2
				Liquid	25.0	0.0	75.0
4	29.0	19.0	52.0	$CuGaTe_2$	27.8	22.8	49.4
				Liquid	40.4	1.9	57.7
5	32.5	15.0	52.5	$CuGaTe_2$	25.7	21.7	52.6
				Liquid	49.3	0.2	50.5
6	42.0	6.0	52.0	$CuGaTe_2$	27.1	19.9	53.0
				Liquid	45.2	1.4	53.4
7	23.0	25.0	52.0	$CuGaTe_2$	24.7	21.8	53.5
				Liquid	5.9	1.2	92.9
8	18.0	26.0	56.0	$CuGaTe_2$	23.7	22.0	54.3
				Liquid	0.6	8.6	90.8
9	12.0	30.0	58.0	$CuGaTe_2$	26.1	22.4	51.5
				Ga_2Te_3	0.0	39.8	60.2
				Liquid	0.5	9.8	89.7
10	11.0	34.0	55.0	$CuGaTe_2$	25.8	20.9	53.3
				Ga_2Te_3	0.0	40.5	59.5
11	10.0	40.0	50.0	$CuGaTe_2$	26.2	22.5	51.3
				GaTe	0.0	50.1	49.9
12	25.0	25.0	50.0	$CuGaTe_2$	24.8	24.4	50.8
13	37.0	15.0	48.0	$CuGaTe_2$	26.9	19.9	53.2
				$Cu_{1.6}Te$	59.1	0.1	40.8
				Liquid	48.6	0.3	51.1
14	48.0	9.0	43.0	$CuGaTe_2$	26.1	22.1	51.8
				Cu_2Te	66.9	0.0	33.1
				$Cu_{1.6}Te$	58.7	0.0	41.3
15	5.0	55.0	40.0	GaTe	0.9	50.1	49.0
				Liquid	5.0	94.9	0.1
16	8.0	52.0	40.0	GaTe	0.1	45.6	54.3
				Liquid	36.2	63.7	0.1
17	5.0	62.5	32.5	GaTe	0.3	50.1	49.6
				Liquid	4.7	95.2	0.1
18	10.0	70.0	20.0	GaTe	0.0	50.6	49.4
				Liquid	21.1	75.8	3.1
19	10.0	80.0	10.0	GaTe	0.0	46.8	53.2
				Liquid	15.8	80.4	3.8
20	30.0	50.0	20.0	GaTe	0.0	45.9	54.1
				Liquid	39.3	60.7	0.0
21	38.0	44.0	18.0	GaTe	0.2	45.0	54.8
				Cu_9Ga_4	65.5	34.5	0.0
				Liquid	46.9	53.1	0.0
22	50.0	45.0	5.0	GaTe	0.8	47.4	51.8
				Cu_9Ga_4	61.2	38.8	0.0
				Liquid	47.9	52.1	0.0
23	61.0	35.0	4.0	GaTe	2.9	48.9	48.2
				Cu_9Ga_4	66.7	33.3	0.0
24	20.0	35.0	45.0	$CuGaTe_2$	26.5	22.0	51.5
				Cu_9Ga_4	66.3	33.4	0.3
				GaTe	2.1	50.5	47.4
25	30.0	30.0	40.0	$CuGaTe_2$	25.7	22.5	51.8
				Cu_9Ga_4	65.1	34.6	0.3
				GaTe	4.4	46.9	48.7
26	35.0	32.5	32.5	$CuGaTe_2$	26.2	22.7	51.1
				Cu_9Ga_4	67.1	32.7	0.2
				GaTe	1.9	45.2	52.9
27	40.0	30.0	30.0	$CuGaTe_2$	26.0	22.4	51.6
				Cu_9Ga_4	66.1	33.6	0.3
				GaTe	7.9	45.2	46.9
28	60.0	30.0	10.0	$CuGaTe_2$	30.7	20.9	48.4
				Cu_9Ga_4	67.6	32.4	0.0
29	42.0	27.0	31.0	$CuGaTe_2$	29.3	19.2	51.5
				Cu_9Ga_4	68.5	30.8	0.7
30	50.0	12.0	38.0	$CuGaTe_2$	27.8	22.4	49.8
				Cu_9Ga_4	71.0	28.8	0.2
				Cu_2Te	66.2	0.1	33.7
31	40.0	20.0	40.0	$CuGaTe_2$	27.9	20.7	51.4

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