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# Solubility and microstructure in the pseudo-binary PbTe–$Ag_2Te$ system

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ABSTRACT

The solvus lines of the PbTe and $Ag_2Te$ phases in the pseudo-binary PbTe–$Ag_2Te$ system have been determined using diffusion couples and unidirectional solidification by the Bridgman method. The solubilities of both $Ag_2Te$ in PbTe and PbTe in $Ag_2Te$ decrease with decrease in temperature. For the former, this change is from 14.9 at% Ag (694 °C) to 0.5 at% Ag (375 °C), while for the latter it is from 12.4 at% Pb (650 °C) to 3.1 at% Pb (375 °C). The decrease in solubilities leads to the formation of precipitates of $Ag_2Te$ in PbTe and PbTe in $Ag_2Te$. In particular, fast atomic diffusion in $Ag_2Te$ results in the precipitation of PbTe even in quenched samples. From the temperature dependence of these solubilities, heats of solution have been determined. In the diffusion couple, the phase boundary moves toward PbTe. In the region between the phase boundary and the initial interface, PbTe transforms to β-$Ag_2Te$ (cubic) retaining the cube-on-cube orientation relationship.


## 1. Introduction

In thermoelectric materials, reducing the thermal conductivity is one of the key ways to improve thermoelectric conversion efficiencies. Microstructure formation with nanometer scales has recently attracted much attention as an effective way to scatter phonons, leading to lattice thermal conductivity reduction [1]. In metals, semiconductors such as thermoelectric materials, and ionic conductors, the electronic [2] or ionic [3] transport properties are largely affected by point defects. The knowledge on phase diagrams is essential for fabrication processes, control of microstructure, practical use at high temperatures, and understanding thermodynamic and point defect properties.

The pseudo-binary PbTe–$Ag_2Te$ system is composed of the excellent thermoelectric materials PbTe and $Ag_2Te$. The thermoelectric properties in the PbTe-rich region have been investigated both within the solid solution range [4–6] and at compositions exceeding the solubility limit, where the lattice thermal conductivity is significantly reduced due to the formation of $Ag_2Te$ precipitates [7]. The morphological evolution of $Ag_2Te$ precipitates as well as the interfacial structure between the precipitates and the PbTe matrix have also been studied [8]. $Ag_2Te$ is also known for the superionic conduction property [9,10] of the β-phase (cubic, space group: *Fm*-3*m*, 145 °C < *T* < 802 °C [11])[1] and the good thermoelectric properties of both the α-phase [14–17] (monoclinic, space group: $P2_1/c$, *T* < 145 °C [11]) and the β-phase [18,19]. PbTe based materials in the "LAST" (lead–antimony–silver tellurides) system are known for their high thermoelectric figure of merit [20], which originates from their nanodot structures. Recently, the nanodots have been found to be consisting of $Ag_2Te$ inclusions [21]. The pseudo-binary PbTe–$Ag_2Te$ system is also an important constituent of the LAST system, particularly since LAST compositions close to the PbTe–$Ag_2Te$ pseudo-binary line show the highest thermoelectric figure of merit. Regardless of the importance of this system, the solubility ranges in the solid states have not been extensively investigated. Fig. 1 shows the phase diagram of the pseudo-binary PbTe–$Ag_2Te$ system. The maximum existence ranges of both the PbTe and the $Ag_2Te$ phases have been determined to be 11 and 52 at% Ag, respectively, by extrapolation of the solidus lines measured by differential thermal analysis down to the eutectic temperature (694 °C) [22]. While the latest assessment of the phase diagram of this system [23] draws broken lines as unknown for the solvus lines for both PbTe and $Ag_2Te$ phases, there is one measured point at 500 °C for the PbTe side and there are several points for the $Ag_2Te$ side [24].

In this paper, we determine the solvus lines for the dissolution of $Ag_2Te$ in PbTe phase and those of PbTe in $Ag_2Te$ in the pseudo-binary PbTe–$Ag_2Te$ system as functions of temperature using $Ag_2Te$/PbTe diffusion couples and unidirectional solidification by the Bridgman method. The determination of solvus lines in this system is essential particularly in controlling the precipitation microstructure and knowing the stability of the precipitates at high temperatures, the thermodynamic properties in the solid solution regions, and the compositions of the matrix phases in the precipitation microstructure, which are connected to the point defect structure and hence thermal and electrical properties.

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[1] Note that we denote the middle temperature $Ag_2Te$ phase (145 °C < *T* < 802 °C) as the β-phase throughout this paper though it is sometimes referred to as the α-phase [10–13].

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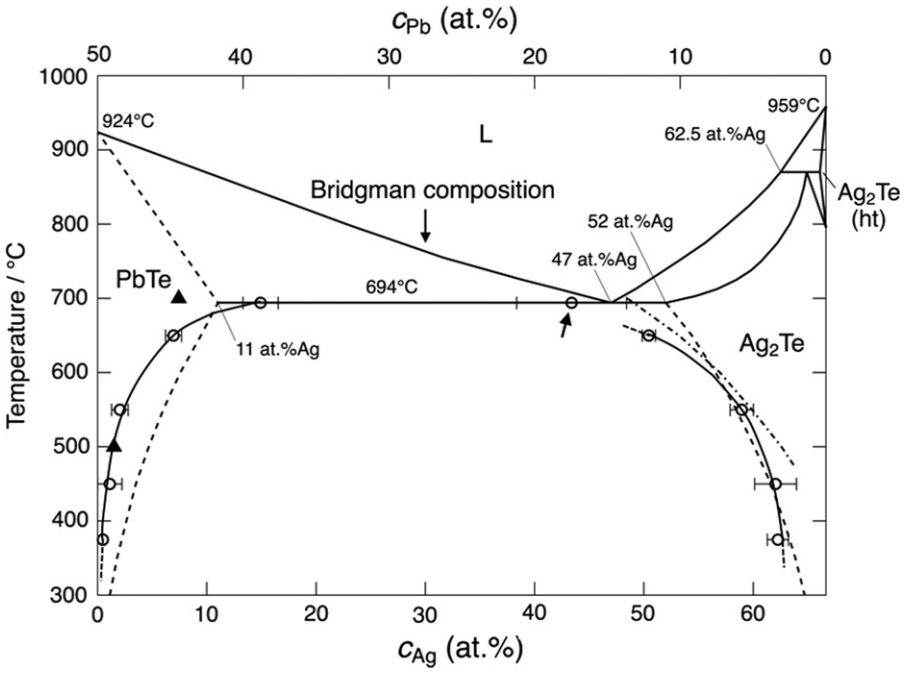


**Fig. 1.** Phase diagram of the pseudo-binary PbTe–$Ag_2Te$ system. Open circles, for which solid curves are drawn, are the solubility ranges for PbTe and $Ag_2Te$ phases determined in this work. The point with an arrow is the eutectic composition measured from the sample unidirectionally solidified by the Bridgman method. Other solid lines are from the assessment by Grieb [24]. Broken lines were drawn as unknown in Grieb's assessment [24]. Dashed-dotted line and triangles are taken from Wald [25].

## 2. Experimental

### 2.1. Diffusion couple experiments.

$Ag_2Te$ and PbTe ingots were synthesized by melting elemental granules of Pb (99.999%, Alfa Aesar), Ag (99.9999%, Alfa Aesar), and Te (99.999%, Alfa Aesar) in carbon coated quartz ampoules filled with 30 kPa of Ar at 950 °C for 10 min. Each ingot weighed 10 g. After melting, the ampoules were quenched in water. They were then annealed at 700 °C for 1 week for homogenization. The homogeneity of the samples was checked by microstructure observation with field emission scanning electron microscopy (FE-SEM, ZEISS 1550 VP).

Diffusion couples between PbTe and $Ag_2Te$ were prepared as follows. The ingots were cut into 3 mm pieces using a low speed diamond saw. One plane of each sample was polished with 9 μm diamond slurry followed by 1 μm slurry on grinding disks to obtain a smooth surface. The polished planes of $Ag_2Te$ and PbTe samples were brought into contact using a stainless steel clamp covered with alumina power. The clamp holding one couple of $Ag_2Te$ and PbTe samples was wrapped in Ti and Ta foil and sealed in a quartz tube with an inner diameter of 22 mm filled with 30 kPa of Ar.

In this study, the phase boundary compositions at various temperatures are determined from the chemical composition profile after annealing at respective temperatures followed by fast cooling. Therefore, the cooling rate must be high enough to retain the chemical composition profiles at the given temperature. In the present system, there were some technical difficulties;

1) PbTe is a fragile material and cooling too fast leads to cracking of the samples,
2) chemical diffusion in this system, especially in $Ag_2Te$, which is known for its superionic conduction of Ag, is so fast that Ag diffusion during cooling could change the chemical composition profile before cooling if the cooling rate is not high enough, and
3) fast diffusion causes solid state precipitation during cooling, which is due to lower solubilities at lower temperatures. This makes it hard to obtain smooth composition profiles if the microstructure size is too coarse.

**Table 1**
Annealing conditions and spot size used in EPMA. For methods of quenching, see text.

| Sample no | Temperature (°C) | Annealing length | Spot size (μm) | Quenching method |
|---|---|---|---|---|
| 0 | 375 | 104 d 20 h | 5 | 3 |
| 1 | 450 | 8 h | 13 | 1 |
| 2 | | 5 d | 15 | 2 |
| 3 | | 20 d | 20 | 3 |
| 4 | 550 | 4 h | 13 | 1 |
| 5 | | 16 h | 13 | 3 |
| 6 | | 64 h | 20 | 3 |
| 7 | | 10 d 16 h | 20 | 3 |
| 8 | 650 | 1 h | 13 | 1 |
| 9 | | 16 h | 12 | 2 |
| 10 | | 64 h | 20 | 2 |
| 11 | Bridgman PbTe region | | 50 | |

Therefore, some different annealing methods were tested. In initial attempts (Method 1, Samples 1, 4, and 8, see Table 1), the samples were annealed with the clamp for the length of the annealing. It was, however, found that this decreased the cooling rate substantially as a lot of heat was retained in the steel clamps even after the quartz ampoule was quenched in water. The large diameter of the ampoule also decreased the heat transfer between the sample and the cooling water. In order to increase the cooling rate, the quartz glass was broken upon quenching in water (Method 2, samples 2, 9, and 10). However, since the samples are very fragile, diffusion couples were prone to cracking with this method due to thermal stresses caused by the rapid cooling. The remaining samples were bonded at 450 °C for 8 h. The heat treatment was terminated by inserting the ampoule into water without breaking it (Method 3, Samples 3, 5, 6, and 7). The diffusion contribution at this temperature and time scale was low.