Microstructural manipulation in GeTe thermoelectric material

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Abstract

Lately, Germanium-tellurides (GeTe) were seen as promising thermoelectric materials with outstanding transport properties. GeTe existing a high carrier concentration due to the presence of Ge vacancies. Thus, GeTe featured with high electrical and thermal conductivity. In recent research, there are several strategies to improve the TE performance. Meanwhile, GeTe suffers a structural transition from rhombohedral α-GeTe to cubic β-GeTe with the rising temperature. Furthermore, the morphology divergence could be achieved by solidification and compositional control. Especially, the equilibrium phase diagram construction which offers a solid path toward microstructural manipulation.

***Keywords -GeTe; phase transition; thermoelectric material; phase diagram; microstructure*.**

The evolution of industrial development accompanies with increasing energy consumption and waste heat emission. In these years, TE materials can be widely used in different areas on temperature-dependent. The conversion efficiency in TE materials can be indicated by a dimensionless figure of merit $zT = \sigma S^2 T/\kappa$ where σ is electrical conductivity, S is Seebeck coefficient, κ is thermal conductivity and T reveal as a specific temperature [1]. Moreover, recent researches are delicate on the improvement of conversion efficiency and the extension of the application temperature region. Therefore, the variation of phase stability, microstructures, and thermodynamic behaviors become more important in TE materials.

Germanium telluride (GeTe) is a heavily *p*-type degenerate semiconductor with a large free charge carrier density of ~ 10^{21} cm^{-3} due to Ge vacancies and featured with high electrical and thermal conductivity is targeted in this research [2]. GeTe undergoes a phase transition between low-temperature rhombohedral α-GeTe and high-temperature cubic β-GeTe with the rising temperature (Fig. 1) [3] which could directly induce the discontinuities in temperature-dependent TE property curves (Figs. 2-3). Moreover, the metallographic observation of GeTe showed a herringbone structure in low-temperature rhombohedral α-GeTe, which is arranged by different orientations in white and black contrast. People consider this particular structure as a reason that reduced thermal conductivity in the previous report [4]. The metallographic of GeTe TE alloy was shown in Fig. 4. In addition, the crystal structures could become more complex if GeTe undergoes a heat treatment since that *P1*, *R3m*, and *Cm* can coexist in crystalline GeTe [5]. Above all, the peak zT value of pristine GeTe is ~ 0.9 at 700 K [6] which makes GeTe-based alloys more attractive.

According to the binary phase diagram (Fig. 1), which can picture the morphology and transport behaviors by the phase distribution [3]. So far, we could implement the microstructural manipulation by solidification and compositional control. The GeTe alloys were fully investigated by material analysis and TE assessment.

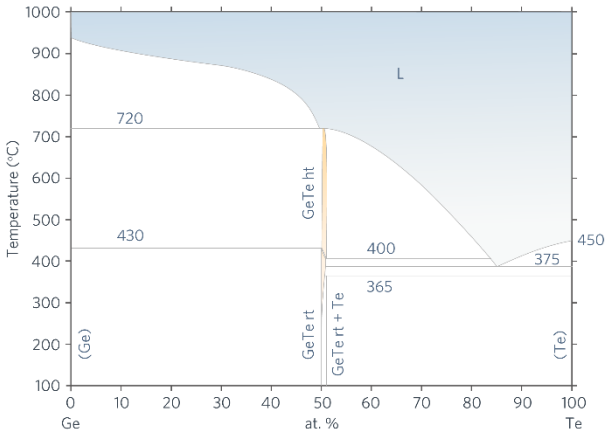

Fig. 1 Ge-Te binary phase diagram [3].

Series of GeTe alloys which solidified through controlled cooling rates were discussed first in Fig. 2 It could lead to the lower lattice thermal conductivity follow up with an enhancement of TE performance base on these situations (Figs. 2-3). With the controlled cooling rates, the zT value could elevate from 0.9 to 1.9 at 723 K. Thus, further research to optimize the TE performance was completed by tuning the stoichiometric composition between Ge and Te.

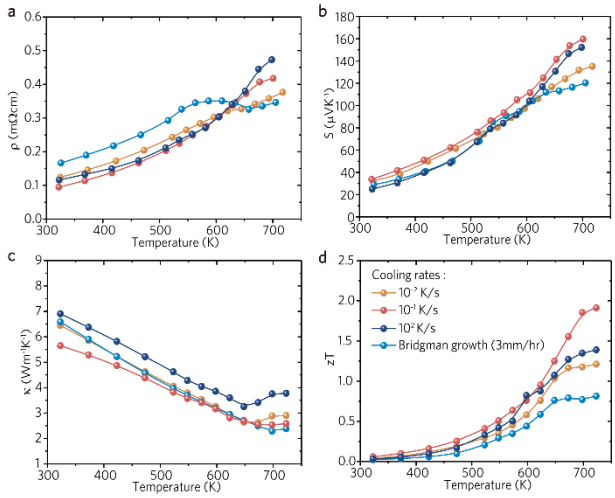

Fig. 2 Temperature-dependent (a) ρ electrical resistivity (b) S Seebeck coefficient (c) κ thermal conductivity (d) zT value of GeTe through controlled cooling rates.

The temperature-dependent measurement results of Ge_xTe_y among the compositional control was shown in figure 3. With the controlled composition, the zT value could elevate from 0.6 to 1.2 at 723 K. The back-scattered electron image (BEI) and the elemental mapping results of the Ge_xTe_y #2 alloy reveal two different contrasts (Fig. 4a), suggesting the existence of two different equilibrium phases. On the basis of compositional analysis and XRD pattern (Fig. 4f), the Ge_xTe_y #2 alloy locates in a two-phases region confined by the α-GeTe and the Ge. Another crucial example is given by Ge_xTe_y #2 alloy (Figs. 4d-e), which showed a herringbone structure which is a typical structure of the GeTe alloy. To identify the crystal structure of GeTe during the phase transition, we had measured the powder XRD (Fig. 4f).

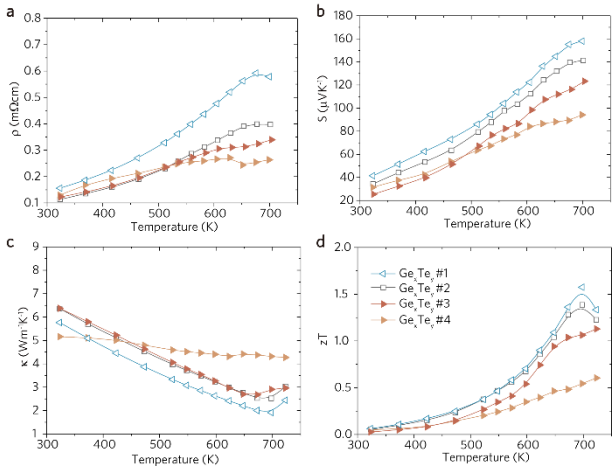

Fig. 3 Temperature-dependent (a) ρ electrical resistivity (b) S Seebeck coefficient (c) κ thermal conductivity (d) zT value of GeTe through compositional control.

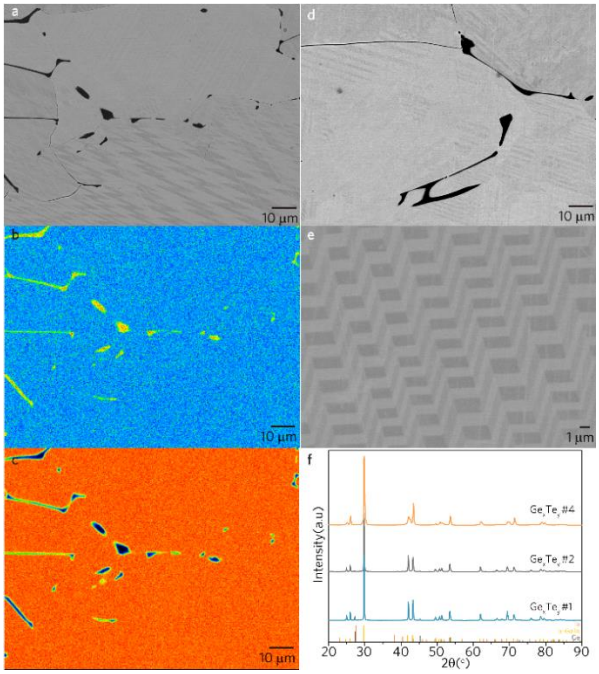

Fig. 4 The metallographic observation of Ge_xTe_y alloys (a) backscattered electron image (BEI) of Ge_xTe_y #2, elemental mapping results from (a) of (b) Ge and (c) Te, (d) backscattered electron image (BEI) of Ge_xTe_y #1 (e) Magnify the BEI from (d), (f) XRD patterns of Ge_xTe_y alloys.

The enhancement of TE performance could be achieved by solidification and compositional control. Through these two strategies could reduce the thermal conductivity and elevate the electric power leading the highest zT ~ 1.9 of GeTe alloy at 723 K.

Acknowledgements

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