Supplementary information: **Specific heat of $(GeTe)_x(Sb_2Te_3)_{1-x}$ (GST) phase-change materials: The impact of disorder and anharmonicity**

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Two topics have been excluded from the manuscript for a more detailed discussion in this supplement:

A) The reversible phase transition observed in the specific heat of GeTe-rich compounds
B) The generic specific heat data of the stable trigonal phase of all compounds from the pseudobinary line

A) Reversible transitions in GeTe and $Ge_8Sb_2Te_{11}$

GeTe possesses a low-temperature trigonal (α) phase with ferroelectric properties and a cubic high-temperature phase. The reversible transition between these two states takes place at a temperature, which depends sensitively on the stoichiometry around the α phase (which has equal atomic fractions of Ge and Te [1]). Ge-rich GeTe transforms at around 700 K, whereas Te-rich GeTe transforms at around 670 K [1].

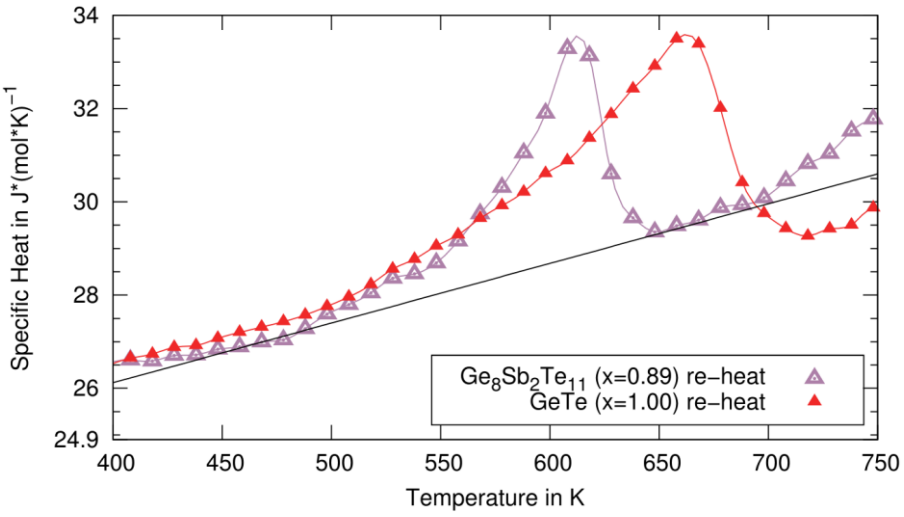

Fig. S1: *The specific heat of GeTe and $Ge_8Sb_2Te_{11}$ shows a reversible feature upon cooling (cf. Fig. S2) and re-heating, which is absent in all other investigated compounds from the pseudobinary line. It can be attributed to a ferroelectric phase transition in those materials. In GeTe, it occurs at 680(10) K upon heating, whereas in $Ge_8Sb_2Te_{11}$, it occurs at 630(10) K.*

Fig. S1 depicts the specific heat measured after annealing the phase-change materials GeTe and $Ge_8Sb_2Te_{11}$ at 788 K and 768 K, respectively. Fully reproducible and hence reversible properties of the phase transition could be obtained during re-heating and subsequent cycles (also cf. Fig. S2). GeTe undergoes a reversible transformation at 680(10) K upon re-heating the sample, whereas $Ge_8Sb_2Te_{11}$ makes a transition at 630(10) K. The shape of the specific heat as a function of temperature corresponds well with that of models for the ferroelectric transition presented in literature (e.g. [2]). The latent enthalpy of this reversible process was determined to 410(25) J/mol and 186(20) J/mol for GeTe and $Ge_8Sb_2Te_{11}$, respectively. These numbers allow calculating the latent entropy of the phase transition and might further help to determine the nature of the ferroelectric phase transition in the light of reports of a displacive [3] and an order-disorder model [4]. Only the vibrational entropy changes during the displacive phase transition, but also the configurational entropy changes during an order-disorder transition.

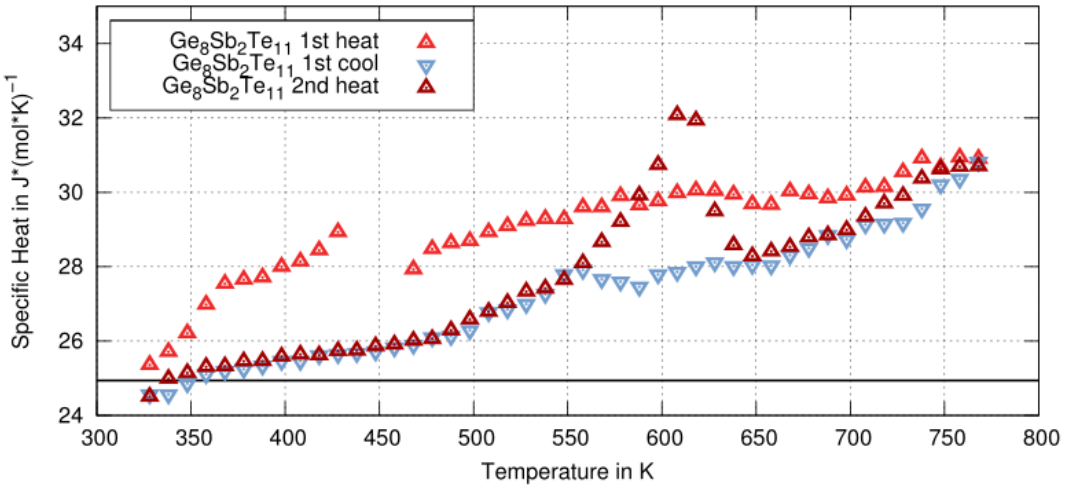

Fig. S2 *depicts the specific situation in $Ge_8Sb_2Te_{11}$, where the mechanism inducing the additional specific heat changes with the annealing condition: During the first heating a large increase is observed over a wide range of temperatures. This mechanism is related to the ordering of vacancies. During the second heating, a well-defined phase transition occurs, which can be attributed to the trigonal to cubic phase transition reported for $Ge_8Sb_2Te_{11}$ [5], albeit at higher temperature. The first cooling process does not show any clear increase in specific heat, but rather follows the generic cooling behavior (cf. Fig. S3).*

B) Generic behavior of specific heat upon cooling

Fig. S3 depicts the specific heat upon cooling of all investigated materials after annealing them to their stable, trigonal phase. Only the specific heats of GeTe and $Ge_8Sb_2Te_{11}$ deviate due to the reversible phase transition in these materials – all other compounds have similar specific heats within +/- 0.3 $J(mol\ K)^{-1}$, which is significantly smaller than the deviations in the meta-stable crystalline phase of +/- 1.5 $J(mol\ K)^{-1}$.

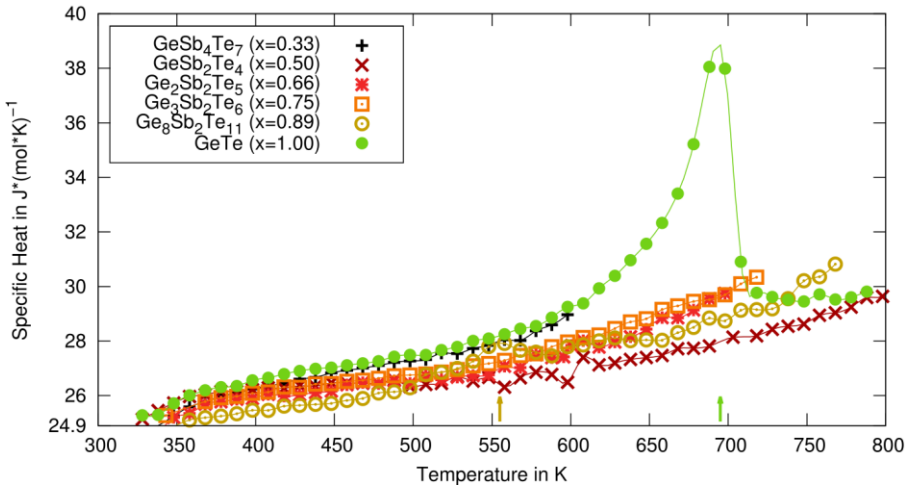

Fig. S3 *shows the cooling curves of all investigated materials in their stable, trigonal phase. This specific heat corresponds to a generic behavior, from which only GeTe and* $Ge_8Sb_2Te_{11}$ *deviate due to their reversible ferroelectric phase transition.*

References

(1) Schlieper, A.; Blachnik, R.; Minerale, D. C. P.; Pharmacie, F. De. Thermodynamic Evaluation of the Germanium - Tellurium System. *Calphad* **1999**, *23*.

(2) Zhang, L.; Zhong, W. Order-Disorder Model in Ferroelectrics. *Phys. Lett. A* **1999**, *260*, 279–285.

(3) Chattopadhyay, T.; Boucherlet, J. X.; von Schnering, H. G. Neutron Diffraction Study on the Structural Phase Transition in GeTe. *J. Phys. C solid state Phys* **1987**, *20*, 1431–1440.

(4) Fons, P.; Kolobov, A.; Krbal, M.; Tominaga, J.; Andrikopoulos, K.; Yannopoulos, S.; Voyiatzis, G.; Uruga, T. Phase Transition in Crystalline GeTe: Pitfalls of Averaging Effects. *Phys. Rev. B* **2010**, *82*, 2–6.

(5) Matsunaga, T.; Morita, H.; Kojima, R.; Yamada, N.; Kifune, K.; Kim, J.; Kobata, M.; Ikenaga, E.; Kobayashi, K. Structural Characteristics of GeTe-Rich GeTe–Sb_2Te_3 Pseudobinary Metastable Crystals. *J. Appl. Phys.* **2008**, *103*, 3511.

(6) Gumbel, E. J. *Statistical Theory of Extreme Values and Some Practical Applications*; U.S. Department of Commerce, National Bureau of Standards, 1954.

(7) Siegrist, T.; Jost, P.; Volker, H.; Woda, M.; Schlockermann, C.; Merkelbach, P.; Wuttig, M. Disorder-Induced Localization in Crystalline Phase-Change Materials. *Nat. Mater.* **2011**, *10*, 202.

(8) Zhang, W.; Thiess, A.; Zalden, P.; Raty, J.-Y.; Blügel, S.; Wuttig, M.; Mazzarello, R. Role of Vacancies in Metal-Insulator Transitions in Crystalline Phase-Change Materials. *Nat. Mater.* **2012**, *11*, 952–956.