

## Bulk synthesis and kinetic stabilization of metastable GST and GBT phases by stress and strain

Matthias N. Schneider and Oliver Oeckler

LMU München, Butenandtstr. 5 – 13 (D), 81377 München

Thin films of multinary chalcogenides  $(\text{GeTe})_n(\text{M}_2\text{Te}_3)_m$  [ $\text{M} = \text{Sb}$  (GST),  $\text{Bi}$  (GBT)] with varying compositions allow to reversibly store and read data due to the change in physical properties associated with the transition between amorphous and metastable cubic crystalline phases.<sup>[1]</sup> The corresponding layered stable modifications are trigonal and must be avoided as they interrupt the write-erase cycle in PCMs, however they might be interesting thermoelectrics.<sup>[2]</sup>

Metastable crystalline GST-PCMs apparently exhibit very simple rocksalt-type average structures with Ge, Sb and voids sharing the cation positions and Te occupying the anion positions. For GeTe-rich compositions such as  $\text{Ge}_{0.8}\text{Sb}_{0.13}\text{Te}$ , this structure is also found as a stable high-temperature modification accessible as a bulk material. This has been shown by in situ temperature powder diffraction experiments on thin film samples<sup>[3]</sup> and recently also by our in situ temperature dependent single crystal diffraction experiments at  $550^\circ\text{C}$  ( $Fm\bar{3}m$ ,  $a = 6.06 \text{ \AA}$ ). Upon rapid quenching, these bulk samples do not transform into the corresponding stable long-periodically ordered structures, but remain pseudocubic and disordered as confirmed by single crystal diffraction on the phase  $\text{Ge}_{0.8-x}\text{Sb}_{0.2}\text{Te}$  ( $x < 0.1$ ,  $R3m$   $a = 4.24$ ,  $\text{Å}$   $c = 10.29 \text{ \AA}$ ,  $R1(\text{obs}) = 0.031$ ) and TEM investigations. The metric distortion along the cubic  $[111]$  direction can be observed as characteristic anisotropic peak broadening in X-ray powder patterns and is most pronounced in finely ground samples. Upon annealing at elevated temperatures (but below the stability region of the cubic modification), finely ground samples readily transform into stable phases, whereas this process is restricted for larger grain sizes. During the phase transition to the stable phases, stress is induced by metric distortion and fourfold twinning as a consequence of symmetry reduction. Relaxation, microstrain and further ordering of voids depend on the grain size. For larger crystallites stress and strain impede the diffusion process needed for the formation of stable long-periodically ordered layered superstructures at moderate temperatures.

This implies that the metastable phases exhibit a higher density than the stable superstructures. This assumption is corroborated by high-pressure experiments on GBT bulk specimens with compositions  $\text{GeBi}_2\text{Te}_4$ . According to powder patterns and electronmicroscopy, compounds with simple cubic average structures have been obtained by quenching melts from  $900^\circ\text{C}$  under a pressure of about 12 GPa.

We assume that the kinetical stabilization of the (pseudo-)cubic phases against phase separation or phase transition involves mechanical factors which might as well play an important role in PCM devices.

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