Kinetic and thermodynamic aspects of crystallization in the phase-change material $Ge_{15}Sb_{85}$

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- Abstract -

Highly doped Sb-based alloys exhibit remarkable properties in terms of switching speed [1] and a strong contrast in electric resistivity of several orders of magnitude [2]. These prerequisites and the inherent tendency towards resonance bonding [3] in the crystalline state render e.g. $Ge_{15}Sb_{85}$ suitable for electronic phase change applications. It has been reported, however, that phase separation occurs at temperatures of about 360°C, leading to the appearance of diffraction peaks of pure Ge. Calorimetric data obtained in this study show the commonly observed endothermic peak of crystallization at 250 °C with a latent heat of 37 J/g and a second endothermic transition at 359(1) °C with a latent heat of 3.6 J/g. EXAFS data were measured on as-deposited amorphous and crystallized $Ge_{15}Sb_{85}$. The crystallization has been performed at 260 °C. For both samples, the K absorption edges of Ge and Sb were measured in transmission geometry at beamline C at Hasylab. The resulting data sets were analysed by fitting calculated scattering paths, which were obtained using the FEFF software. In an additional calculation, a custom made RMC code was employed to obtain an atomic model that is compatible with the measured EXAFS data. A determination of bond lengths shows that there is only one Ge-Ge bond length of 2.46(2) Å in amorphous $Ge_{15}Sb_{85}$, while the data of crystallized $Ge_{15}Sb_{85}$ are dominated by a superposition of two Ge-Ge bond lengths (2.43(1) Å and 2.79(8) Å). This superposition indicates that there is a contribution by pure Ge (2.43(1) Å) and some Ge atoms occupying neighbouring lattice sites of Sb (2.89 Å). This finding is a direct indication of phase separation in $Ge_{15}Sb_{85}$, which takes place during the crystallization of the Sb-rich phase and leads to a segregation of a Ge-rich, amorphous phase, which subsequently crystallizes at 359(1) °C.

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