Melting and freezing of Bi Nanoclusters Embedded in Glass

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Bi-glass nanocomposites were obtained by quenching homogeneous Bi-doped soda-borate melts followed by an annealing at $T = T_a$. This process induces the formation of spherical Bi nanoclusters embedded in a glass matrix [1]. Since $T_a \geq T_{mb}$, T_{mb} being the melting temperature of bulk Bi, we have in fact obtained liquid Bi droplets that, after cooling, became spherical nanocrystals. The nanocrystal-to-liquid transition was investigated using simultaneously the SAXS and WAXS techniques [2]. The melting temperature T_m decreases for decreasing radius and is a linear function of $1/R$, $T_m=T_{mb}–a/R$, a being a positive constant related to surface energy parameters. For Bi nanocrystals with R = 1.5 nm, the magnitude of the melting temperature reduction is about 200 K. An additional study of the liquid-to-crystal transition was performed. The freezing temperature of bulk Bi, T_{cb}, is much lower than T_{mb}, (T_{mb}-T_{cb}=150 K). We have established that the freezing temperature also decreases linearly for increasing values of ($1/R$), but at a rate lower than the melting temperature, in such a way that the magnitude of the overcooling is progressively reduced for nanodroplets with decreasing radius. The overcooling vanishes for droplets with radius close to 2 nm. The linear nature of T_c vs. $1/R$ is explained by using a simple thermodynamic model of heterogeneous crystal nucleation at the liquid-glass interfaces.

[1] Kellermann G., Craievich A. F., *Phys. Rev*. B, 2003, **67**, 085405. [2] Kellermann G., Craievich A. F., *Phys. Rev*. B, 2002, **65**, 134204.

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