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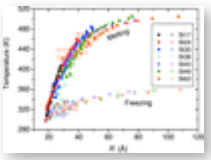

Melting and freezing temperatures of confined Bi nanoparticles over a wide size range

H. F. Degenhardt, G. Kellermann and A. F. Craievich

The size dependences of the melting and freezing temperatures, T_m and T_f, respectively, of spherical Bi nanoparticles embedded in a sodium borate glass were determined by applying a new experimental procedure based on the combined and simultaneous use of small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS). This experimental procedure is particularly useful for materials in which a widely polydisperse set of nanoparticles are embedded. The results provide additional and stronger evidence supporting the main previous conclusions: (i) the melting and freezing temperatures both decrease linearly for increasing reciprocal radius ($1/R$); and (ii) the effect of undercooling is suppressed for Bi nanoparticles with radii smaller than a critical value equal to 1.8 nm. These results confirm a previously proposed low-resolution structural model for Bi nanocrystals below their melting temperature and with radius $R > 1.8$ nm, which consists of a crystalline core surrounded by a disordered shell. In the present work, a number of samples with different and partially overlapping radius distributions were studied, allowing the determination of $T_m(R)$ and $T_f(R)$ functions over a wide range of radii ($1 < R < 11$ nm). Comparison of the experimentally determined $T_m(R)$ and $T_f(R)$ functions corresponding to different samples indicates good reproducibility of the experimental results. This allowed the verification of the robustness of the experimental procedure based on *in situ* combined use of SAXS and WAXS for determination of the radius dependence of the melting and freezing temperatures of spherical nanoparticles in dilute solution.

Keywords: **small-angle X-ray scattering**; **nanocrystals**; **wide-angle X-ray scattering**; **melting**; **crystallization**; **nanoparticles**.