

*Radius-dependent transition temperatures of spherical Bi nanoparticles*Aldo Felix Craievich¹, Hermann F. Degenhardt², Guinther Kellermann²¹Applied Physics Department, Physics Institute, Sao Paulo University, Sao Paulo, Brazil, ²Physics Department, UFPR, Curitiba, Brazil
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The radius dependences of the melting and freezing temperatures, $T_m(R)$ and $T_f(R)$, respectively, associated with size-polydisperse and dilute sets of spherical Bi nanoparticles embedded in a sodium-borate glass, were previously determined by applying an experimental method based on combined and simultaneous use of small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) techniques [1]. This procedure combines size information from analyses of SAXS curves and determinations of temperature-dependent fractions of crystalline volume derived from integral values of Bragg peaks in WAXS patterns. For dilute sets of nanoparticles with approximately same size, an alternative and simpler procedure can be applied, which requires only SAXS measurements of several samples each of them containing nanoparticles with different average radius [2]. Previous determinations of the radius dependences of melting and freezing temperatures of Bi referred to nanoparticles with radii varying from 1 nm up to 4 nm circa [1]. The present study aims at obtaining additional and stronger evidences regarding the conclusions derived from previous work [1]. This purpose was expected to be achieved by determining the radius dependences of the melting and freezing temperatures of spherical Bi nanoparticles over a radius range much wider than in previous work. Thus, we have studied a series of samples containing dilute and size-polydisperse sets of spherical Bi nanoparticles embedded in a sodium-borate glass, the sets of nanoparticles in each sample having different average radius, and wide - partially overlapping - radius distributions. SAXS and WAXS measurements were conducted at the Brazilian National Synchrotron Light Laboratory (LNLS). The simultaneous SAXS and WAXS measurements were performed in situ, on sample heating and cooling cycles, using a specially designed high-temperature chamber [3] and two independent position sensitive X-ray detectors. By combining the results derived from SAXS and WAXS measurements referring to seven different samples, we have determined the radius dependences of the melting and freezing temperatures of spherical Bi nanoparticles with radii ranging from 1 up to 10 nm, that is, over a radius range much wider than in previous work. The results of SAXS/WAXS studies of a series of samples covering a wide radius range provided additional and stronger evidences supporting previous main conclusions, namely (i) the temperatures of melting and freezing of spherical Bi nanoparticles both decrease linearly for increasing reciprocal radius ($1/R$), and (ii) the effect of undercooling is absent for Bi liquid nanodroplets with radius smaller than a critical value $R_c=1.8\text{nm}$. The observed agreements of $T_m(R)$ and $T_f(R)$ functions derived from measurements corresponding to different samples, with partially overlapping radius ranges, indicated a good reproducibility of the experimental results and, consequently, established the robustness of the method that combines information derived from SAXS and WAXS. This SAXS/WAXS procedure is particularly useful for studies of very dilute and size-polydisperse sets of nanoparticles for which the classical alternative method, based on size analysis of usually weak WAXS Bragg peak profiles, does not provide precise results.

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