The Size-Dependent Ferroelectric Phase Transition in $BaTiO_3$ Nanocrystals Probed by Surface Plasmons

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Understanding the fundamental aspects of nanoscale ferroelectricity is important for various applications of ferroelectrics, such as non-volatile memories, pyroelectric and piezoelectric devices. At the nanoscsale, in particular at nanocrystals (NCs) that are strongly confined, deviations from bulk properties are expected due to stronger depolarization fields. This leads to the idea of a critical correlation volume below which ferrolelectricity cannot be sustained. Reports of the size dependent phase transition properties encompass a broad range of results and suggest a drop in Curie temperature with decreasing size. As NC size decreases and the surface layer takes a substantial part of the volume an average over surface and interior would be measured using techniques such as XRD and Raman scattering. Thus, in order to probe the phase transition at the nanoscale, a different method selectively sensitive to the surface of the ferroelectric NCs should be used. A technique for probing the temperature dependence of the dielectric constant of ferroelectric NCs using shifts in the localized surface plasmon resonance wavelength of gold nanoparticles attached to the surface of the ferroelectric NCs is demonstrated. We study the ferroelectric-to-paraelectric phase transition of Barium Titanate (BTO) nanocubes in three size regimes. Temperature-dependent Raman spectroscopy was applied to probe the whole volume of the NCs. It was revealed that $\sim$ 16nm BTO NCs were dominated by surface effects, and as the NC size increased bulk BTO behavior governed. This work strengthens the concept of having different surface and interior, bulk-like contributions to the ferroelectricity and to the phase transitions. It thus indicates on the absence of an intrinsic size-dependence of the transition temperature. In addition the surface ferroelectricity behaves differently from the bulk-like ferroelectricity and is characterized by long relaxation time scales.