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Monitoring the Surfactant Coverage on Ferroelectric Particle during a Ball Milling Process

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Abstract

Ferroelectric nanoparticles can enhance the properties of liquid crystals, increasing the key parameters such as clearing point, birefringence and dielectric anisotropy [1-3]. However, it is also true that reliably producing ferroparticles and the resulting liquid crystal colloids has proven to be a great challenge. One important variable that need to be carefully monitored and controlled is surfactant concentration. Excess surfactant molecules suppress the order parameter of the liquid crystal and masking the effect of the ferroelectric particles. On the other hand, less than enough surfactant coverage results in poor stability of the suspension and big aggregates that would induce defects in the LC.

Here we report on machine milling BaTiO₃ and how varying the preparation conditions, such as surfactant (oleic acid in our case) concentration and milling time, affects the particles surface coverage. The strong C=O stretch of oleic acid serves as a convenient probe for quantitative FTIR (Fourier Transformed Infrared Spectroscopy) analysis. We monitor the absorption peak of C=O appearing at ~1700 cm⁻¹, ~1750cm⁻¹, ~1500-1600cm⁻¹ that are for oleic acid present as a dimer, monomer, or complex conjugate with BaTiO₃, respectively [4]. During grinding, the particle size decreases and the total surface area increases. As a result, more oleic acid molecules bond to the particle so the ratio of the two absorbance, A_{1700} / A_{1550} declines with milling time, and at a certain point reaches a minimum that remains constant with further milling. The minimum occurs when the particle surface is completely covered and no freely suspended oleic acid molecule remains. The higher the oleic acid concentration, the longer the grinding time (i.e. smaller particle size, and larger total surface area) required for the transition to occur.

Using DSC, we also investigated the ferroelectricity of milled BaTiO₃ particles by measuring the Curie transition of the ferroelectric to paraelectric phase. We observed that the T_{Curie} first increases with milling, reaches its peak value and declines after further milling. We think that the reduction of Curie transition at long grinding hours is due to the particle size decreasing below the the critical size required to preserving ferroelectricity[6]. The enhancement of the Curie peak at the early stage of grinding might be associated with breaking down the aggregates and narrowing of the size distribution of ferroelectric particles. The maximum T_{curie} is dependent on the oleic acid concentration. Currently, we are trying to synchronize the surfactant transition point with the maximum T_{curie} in order to optimize the ferroelectricity with surface coverage simultaneously. We believe the FTIR is a powerful tool to identify and quantify the state of oleic acid or other carboxylic acid type of surfactant, which is important for optimizing the properties of nanoparticle dispersions in general.

References

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