

# Static and Dynamic Electric and Magnetic Imaging

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### Phase shift of single-domain ferroelectric nanoparticles

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Capturing with electron phase sensitive techniques the vacuum electric field that is expected to surround polarized particles has proven to be extremely challenging. On one hand, considering the very large spontaneous polarization of typical ferroelectric materials, and based on a formal analogy with ferromagnetic nanoparticles, one may intuitively expect the phase shift to be very large and the experiments straightforward. On the other hand, in spite of numerous attempts in various electron microscopy facilities worldwide, only hints of a ferroelectric signal from nanoparticles (NPs) are present in the literature (see in particular the recent article [1] reporting on 15 nm Barium Titanate nanocubes studied by electron holography), highlighting the extreme complexity of the matter.

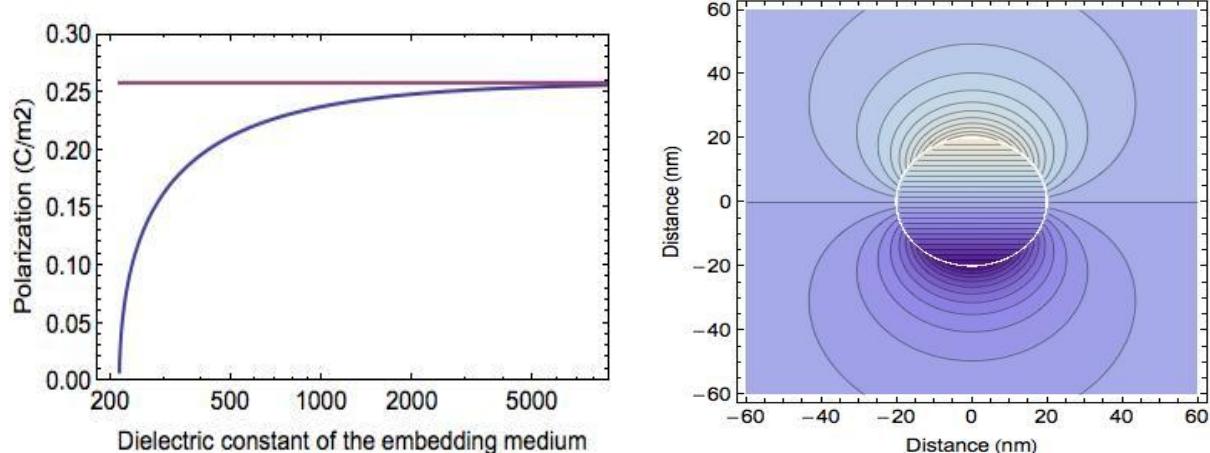
The fundamental reason behind the difficulties in detecting ferroelectric signals from NPs is that  $P$  is suppressed by the depolarizing field, so that a NP made of a material which is ferroelectric in bulk form, loses its  $P$  and is forced into a paraelectric phase. Single-domain ferroelectric NPs, therefore, cannot exist unless depolarization field are compensated. Screening charges from either surface states (generally with metallic character) or nearby conductive elements such as a metallic support, contacts, or electrodes, or, possibly, a surrounding matrix if the NPs are embedded, may provide a relief of the electrostatic energy that suppresses  $P$ , so that some degree of polarization survives. Furthermore, differently from ferromagnetic materials, the ferroelectric domain size has no lower bound other than the unit cell, so that the natural anti-ferroelectric nature of dipolar interactions, i.e. the tendency to form domains of opposite polarization in order to lower the energy, is not countered by balancing driving forces (for example: the wall energy cost associated with the formation of 180° domains along the polar direction is very small) and further decreases the net  $P$  of NPs [2].

We present here an estimate of the electron-holographic signal (phase shift) we may expect from a spherical particle made of a material that is ferroelectric in bulk form. We use barium titanate (BTO) as reference material since its bulk ferroelectricity is well described by a set of known coefficients for the free energy. The polarization-related free energy density term describing a crystal that undergoes a paraelectric-ferroelectric transition [3] is  $F=-(A/2)P^2+(B/4)P^4+(C/6)P^6$ , with  $(A,B,C)$  known temperature-dependent coefficients [4]. By minimizing the free energy, we find that as long as  $A>0$  a spontaneous polarization appears with a value determined exclusively by the three coefficients. For BTO, this value at room temperature equals  $P_s=0.26 \text{ C/m}^2$ , its bulk polarization. As soon as a particle is made out of bulk BTO, however, an extra term has to be added to its free energy: the electrostatic energy of the polarization charge density established at the surface of the object. If the object is carved out in the form of a sphere, or a solid with an equivalent symmetry (cube, etc.), then the depolarization field energy density equals  $P^2/(6\epsilon_0)$ : the coefficient of the  $P^2$  term in  $F$  then changes from  $A$  to  $A-A'=A-1/(3\epsilon_0)$ . Since  $1/(3\epsilon_0)$  is about two orders of magnitude larger than  $A$ , the immediate result is that the energy minimum that gave us  $P_s$  disappears: the particle cannot sustain any finite value of  $P_s$ , and is forced back to an unpolarized (paraelectric) state. The only way to restore a finite value of  $P_s$  is to provide means to relieve this huge extra energy preventing ions from displacing inside the unit cell in the way they would do if surfaces and surface charges were not present. We examine here only the effect of embedding the particle in a dielectric matrix of relative constant  $\epsilon_r$ . In such situation, the energy density is  $P^2/[2\epsilon_0(1+2\epsilon_r)]$ , so that, if  $\epsilon_r$  is sufficiently large,  $A-A'$  might remain positive, and the energy minimum that allows a finite  $P_s$  is preserved. The  $P_s(\epsilon_r)$  curve shown in Figure 1 illustrates that the polarization onset occurs at  $\epsilon_r=214$ , and that the residual polarization approaches the bulk value with a  $P_s(1-a/\epsilon_r)$  dependence ( $a\sim 73$ ). The curve also highlights the needs for a high- $k$  dielectric as embedding matrix: anything less effective will kill the polarization.

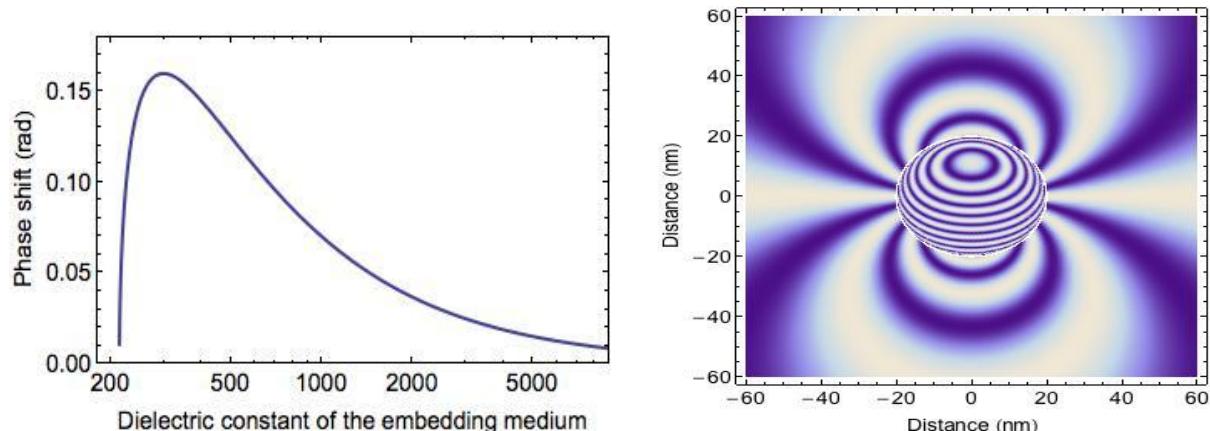
There is another complication. Lorentz deflection of electrons is proportional to the electric field  $E$ , not to  $P$ . Hence, the signal is large when  $E$ , i.e. the depolarization field is large. But when the depolarization field is large,  $P$  is suppressed, so  $E$  vanishes. On the other hand, when the surrounding dielectric provides compensation of the depolarization field, it allows  $P$  to be large, but keeps  $E$  small. In the end, the signal is then going to be small either way. Figure 2 shows the effect of the surrounding

dielectric matrix on the phase shift of a polarized spherical (radius=20 nm) BTO nanoparticle: the plot of the maximal phase shift (two times the phase value at  $r=R$ ) illustrates that in absence of sufficient dielectric screening, the signal vanishes; it then raises in the interval ( $214 < \epsilon_r < 300$ ), and finally drops again because the depolarization field is compensated. The largest possible phase shift we may expect from a single-domain BTO NP embedded in a dielectric matrix is about  $400 * R[\text{nm}]^2 / \epsilon_r$  rad when  $\epsilon_r = 300$ , which is 0.16 rad (or  $\sim 0.16/20$  rad) for a 20 nm radius NP. For comparison, if the same BTO NP was polarized with the bulk value, and dielectric screening was not needed to maintain a finite  $P$ , the expected phase shift would be around 50 rad, more than 300 times larger. Figure 2 confirms that, indeed, detecting ferroelectric signals from NPs is extremely challenging, and that there is a very narrow margin for finding suitable experimental conditions.

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**Figure 1.** Left: polarization of a hypothetical single-domain BTO nanoparticle as a function of the dielectric constant of the embedding medium; the polarization vanishes below a critical value of  $\epsilon_r=214$ . Right: contour plot of the cross-sectional electrostatic potential within and around a polarized BTO NP embedded in a dielectric matrix with  $\epsilon_r=300$ ; equipotentials are at 50 mV.



**Figure 2.** Left: phase shift of a hypothetical single-domain BTO nanoparticle with 20 nm radius as a function of the dielectric constant of the embedding medium; the phase shift vanishes when  $\epsilon_r < 214$ , reaches a maximum at  $\epsilon_r = 300$ , and decreases for higher values of  $\epsilon_r$  due to the compensation of surface charges (the physical source of phase shift). Right: cosine-map (256x amplified) representation of the phase shift for a BTO NP when  $\epsilon_r = 300$  with the effect of the mean-inner-potential (MIP) added to that of the polarization; the particle radius is 20 nm, the accelerating voltage 300 kV, and the MIP 1 V.