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Elucidating the mechanism for indentation size-effect in dielectrics

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Recent work presented experimental evidence of a strong elastic indentation size-effect in ferroelectric $BaTiO_3$. The apparent elastic modulus was shown to exhibit significant stiffening with decreasing contact size and this was attributed to the phenomenon of flexoelectricity. There is however room for debate whether domain wall movement, nucleation, and related phenomena are responsible for the size-effect in $BaTiO_3$. In this work, we present a nanoindentation study of paraelectric $SrTiO_3$ and argue that indeed flexoelectricity rather than ferroelectric-specific effects cause the observed size dependent behavior. © *2012 American Institute of Physics*.
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The phrase indentation size effect is associated with the change in hardness and/or elastic modulus values with the change in indentation depth. In the context of metals, the size-dependent hardness has been extensively researched and is usually attributed to dislocation related activities.[1–4] The general consensus, however, is that elastic modulus does not measurably change with size. This is consistent with atomistic calculations conducted on a wide range of materials.[5] Our recent work on $BaTiO_3$[6] suggested an *elastic* electromechanical indentation size effect. Essentially, the apparent elastic modulus of $BaTiO_3$ noticeably increased with decreasing indentation contact radii. This peculiar elastic size-effect was attributed to the phenomenon of *flexoelectricity*. A theoretical model based on this phenomenon (while approximate) certainly confirmed the observed experimental trends.[6,7] Flexoelectricity refers to the linear coupling between strain gradients and electric polarization and is represented by a fourth order coupling tensor

$$P_i = d_{ijk}\varepsilon_{jk} + f_{ijkl}\frac{\partial \varepsilon_{jk}}{\partial x_l}. \quad (1)$$

Here **d** is the third rank piezoelectric tensor, **f** is the fourth rank flexoelectric property tensor, and ε is the strain tensor. It is interesting to note that, as evident from both theoretical arguments and physical rationalization, flexoelectricity is a universal phenomenon and exists in all crystalline dielectrics including centrosymmetric ones where piezoelectricity is absent.[8,9] While symmetry arguments indicate that flexoelectricity is always present, its magnitude is usually quite small. The strength of the flexoelectricity coupling appears to roughly scale with the dielectric susceptibility and therefore has been found to be quite appreciable in ferroelectrics

$$f \sim \gamma\chi\frac{e}{a}, \quad (2)$$

where e is the fundamental charge, a is the lattice parameter, and γ is a constant. The value of e/a for most materials is about 10^{-10} C/m,[9–11] therefore explaining the prominence of flexoelectricity in strongly dielectric ferroelectric crystals. In the case of $BaTiO_3$ ($f \sim 10^{-5}$ C/m).[12] Clearly, as far as indentation is concerned, the influence of flexoelectric effects during indentation should become more pronounced at small indentation depths where strain gradients are larger. Flexoelectricity appears to be responsible for several intriguing consequences, e.g., "giant" electromechanical coupling at the nanoscale,[13] creation of apparently piezoelectric materials without using piezoelectric materials,[14–17] and unusual electromechanical coupling in nanostructures.[18] Our indentation experiments on the benchmark peizoelectric (but non-ferroelectric) material, quartz,[6] revealed the absence of the elastic size-effect (down to contact radii of 20 nm), strengthening the assertion that flexoelectricity is indeed the cause of the indentation size-effect in $BaTiO_3$—it is to be noted that quartz, a low dielectric constant material, has flexoelectric coefficients that are several orders of magnitude less than that of $BaTiO_3$.[11] The theoretical model developed based on flexoelectricity,[6,7] although approximate, exhibited the experimental trends observed in the experiments. However, there is room for doubt in attributing flexoelectricity as the mechanisms behind the indentation size effect in $BaTiO_3$. While it can be argued that dislocation activity is not likely to be dramatically different between $BaTiO_3$ and quartz (and therefore their contribution is most likely marginal), domain wall movement, nucleation of new domain walls, and related effects cannot be ruled out. To settle this, we conduct a nano-indentation study on a high-dielectric constant material that is paraelectric but has a high flexoelectric coefficient: $SrTiO_3$.

Strontium titanate, at room temperature, is a cubic perovskite belonging to the centrosymmetric point group m3m and hence does not exhibit ferroelectric behavior. Moreover, the flexoelectric properties of $SrTiO_3$ are known from bending experiments to be on the order of $10^{-9} - 10^{-8}$ C/m[19]—in other words significantly more flexoelectric than quartz but less so as compared with $BaTiO_3$.

A series of nanoindentation tests were carried out on (001) oriented single crystal ($5 \times 5 \times 1\,\text{mm}^3$) $SrTiO_3$ using a Berkovich indenter with the continuous stiffness measurement (CSM) technique and a commercial nanoindentation system (Nano Indenter XP, MTS Nano Instruments, Oak

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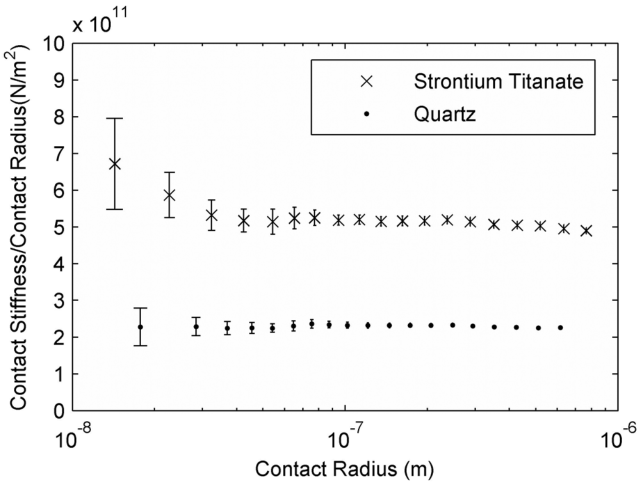

FIG. 1. Variation of contact stiffness of $SrTiO_3$ as a function of contact radii.

Ridge, TN). Indentation loads were applied for a constant strain rate of 0.05 s^{-1} up to the maximum displacement depth of 400 nm. The test results are shown in Figure 1 with the error bars representing one standard deviation at each data point. Note that as with the previous work,[6] the contact radii are in fact effective values calculated from $\pi a^2 = A(h_c)$, where $A(h_c)$ is the calibrated indenter area function.

As evident, an elastic indentation size effect of the type observed in $BaTiO_3$[6] is also present in $SrTiO_3$. The contact stiffness ($\frac{s}{a}$) increases at very small contact radii. For contact radii greater than about 40 nm, the value of $\frac{s}{a}$ essentially asymptotically converges to its bulk value. We can draw two conclusions from this data. First, the size effect demonstrated in $SrTiO_3$ affirms that flexoelectricity is the dominant mechanism—since in the latter, there are no prospects of domains and related phenomena. Consistent with the smaller magnitude of flexoelectric properties of $SrTiO_3$ as compared with $BaTiO_3$, the size-effect in the former is less pronounced. The absence of ferroelectric domains and bulk piezoelectricity in room temperature $SrTiO_3$ preclude their contribution to the observed size effect.

The second major implication of the $SrTiO_3$ data in Figure 1 is that comparative estimates of flexoelectric properties may be possible based on the nature of the size effect, e.g., $SrTiO_3$ is more flexoelectric than quartz. The flexoelectric indentation model previously employed with $BaTiO_3$ data[6,7] is not applicable to non-piezoelectric crystals (since the model is based on perturbation method that uses the classical-piezoelectric solution as a starting point) and so there are no analytical results to compare with the present $SrTiO_3$ data. Nevertheless, based on nano-indentation data, one may deduce the relative magnitudes of the flexoelectric constants of different dielectric crystals. In that sense, nano-indentation could be used as a quick and easy litmus test for selecting materials as candidates for more precise (and time-consuming) methods of flexoelectric characterization.

It is worthwhile to comment on the applicability of the present approach to study temperature-dependent effects. While, in general, temperature effects are somewhat difficult to study experimentally, the simplicity of the indentation approach is likely to make it simpler to carry out as compared to complex bending experiments. As example, recent work by Morozovska *et al.*[20] discusses a very interesting effect in $SrTiO_3$: surface polar states below 105 K due to the so-called flexo-roto effect. We expect that the roto-flexo effect will indeed manifest itself in the elastic stiffness of nanostructures. This exotic phenomenon could potentially be investigated via the indentation technique (notwithstanding the challenges of conducting the experiments at such low temperatures).

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