Absence of ultra-high pressure ferroelectricity in $PbTiO_3$

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Ferroelectricity was long thought to disappear at high pressures, but density functional (DFT) calculations showed reentrant ferroelectricity at high pressures in perovskites such as $BaTiO_3$ and $PbTiO_3$ (PTO). Our second-harmonic generation measurements, however show no evidence of ferroelectricity at ultra-high pressures (above 20 GPa) in PTO. Our DFT computations confirm an absolute static ferroelectric ground state for pressures up to at least 100 GPa. However, the ferroelectric well is very shallow, and we find that PTO is most likely a quantum paraelectric at high pressures with a distorted perovskite crystal structure. This settles a long-time problem in understanding ferroelectric behaviour.

For many years it was thought that ferroelectricity (FE) was squeezed out at high pressures. Room temperature Raman measurements showed a soft mode with increasing pressure that goes to zero at a pressure Pc, with no first-order Raman above this pressure [1-3]. However, first-principles Density Functional Theory (DFT) computations for $PbTiO_3$ showed a series of high pressure phase transitions to other polar phases rather than a simple tetragonal ferroelectric to cubic paraelectric transition [4]. This was confirmed by Raman and micro-x-ray studies that agreed well with experiments at cryogenic temperatures [5]; the earlier observed transition at room temperature is not the ground state. The Ahart et al. study also showed that the low temperature transitions are like the morphotropic phase boundary in $PbTiO_3$-$PbZrO_3$ (PZT) and other ferroelectric solid solutions, but in a pure material, and supported the role of polarization rotation for large piezoelectric response in relaxor ferroelectrics [6]. Theoretical study of perovskite ferroelectrics was pushed to higher pressures, and showed reentrant ferroelectric to ultrahigh pressures [7-9]. This was a surprising result, since in the ferroelectric state atoms move closer together, and the repulsive forces should increase rapidly with density, so that one would expect ferroelectric distortions to be unstable at high pressures, rather than showing increasing instability as predicted by Kornev et al. within DFT. This prediction of ultrahigh pressure ferroelectricity is addressed here using experiments and theory.

To clarify whether the high-pressure ferroelectricity exists or not in PT, we performed Second Harmonic Generation (SHG) measurements (Fig. 1). The second nonlinear harmonic of the dielectric permittivity is finite only if the crystal symmetry is broken such that the crystal does not possess a center of symmetry [26]. The relative intensity at each pressure is obtained by normalizing the integral intensity to the intensity obtained at ambient pressure, during the same time interval. All three runs of experiments (single crystals and powder samples) show consistent results. The SHG signal decreases with pressure almost linearly in the interval between 0 and 12 GPa, but remains almost same above 12 GPa up to 100 GPa with low intensity.

To better understand the discrepancy between DFT computations and our SHG measurements we have performed a large number of DFT computations using different codes, pseudopotentials, and compared also with all-electron computations performed with the WIEN2K code. All static computations are consistent with a ferroelectric ground state, as in previous computations. All these computations cannot prove that there is not a lower static energy structure. For example, there could be a larger unit cell with antiferroelectric (AFE) distortions that would have off-centering, but in an alternating pattern with zero polariza-

tion [10]. We searched for such structures, but exhaustive searching was not able to find a more stable centrosymmetric structure.

A FPMD simulation at 100 GPa seems to give a disordered perovskite structure. Averaging atomic positions over several ps gives a structure that cannot be mapped onto any structure with symmetry greater than P1. This indicates unit cell disorder in polarization direction, consistent, with the low energy barriers for polarization rotation or displacement direction. To confirm this, we computed the Berry's phase polarization and obtained zero polarization, consistent with the SHG measurements.

Our cryogenic SHG measurements also show no signal at high pressures, suggesting that quantum fluctuations also play a role. To test this we mapped the double well from R-3c to R3c at fixed volume, where the central R-3c point at 0 is at 100 GPa. We treat this as a quantum anharmonic oscillator. The zero point energy computed for this oscillator is comparable to the enthalpy difference between R3c and R-3c at 100 GPa. So we expect quantum fluctuations to average over the double well. So our results are consistent with the ground state of ultrahigh pressure PTO being a quantum paraelectric, consistent with experiment.

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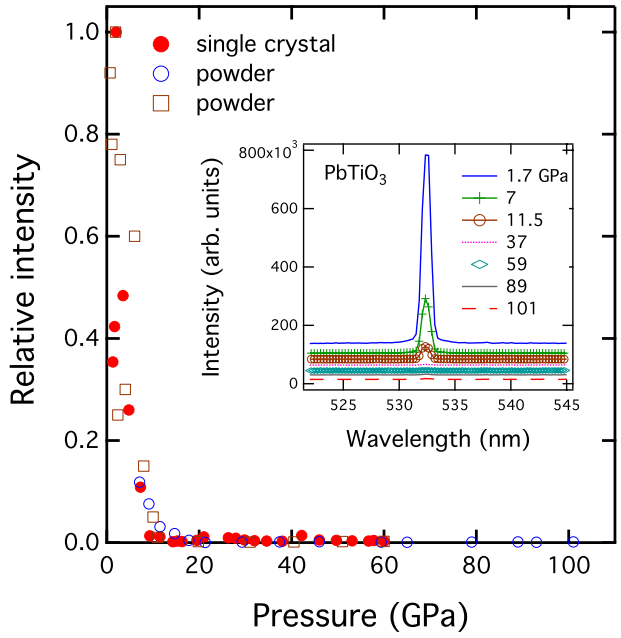

Figure 1. Pressure dependence of the integrated intensity of SHG. We normalize the integrated intensity with the intensity obtained at ambient pressure. We performed three experimental runs: first run, solid circle (red) marks, neon pressure medium; second run, open circle (blue), single crystal, neon pressure medium; third run, solid square (green) marks, neon pressure medium. The SHG spectrum of the $PbTiO_3$ single crystal at selected pressures. The wave length of the incident light is 1064 nm, so the SGH signals appear at 532 nm.

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