Re-emergence of a polar instability at high pressure in $KNbO_3$

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Abstract

Ferroelectricity in perovskites is generally suppressed under moderate hydrostatic pressure, yet first-principles calculations have long predicted a re-emergence of the polar instability at higher pressures. Experimental confirmation of this prediction has remained elusive. Here, we investigate the high-pressure behaviour of the lead-free ferroelectric perovskite $KNbO_3$ up to 63 GPa using single-crystal X-ray diffraction at the ESRF and SOLEIL synchrotron sources, complemented by Raman and infrared spectroscopy and second-harmonic generation (SHG) imaging. Following the known ferroelectric-to-cubic transition near 14 GPa, we identify two further high-pressure phase transitions. At 37 GPa, the emergence of superlattice reflections at the R point signals a transition to a tetragonal I4/mcm phase with anti-phase octahedral tilts. At 44.6 GPa, incommensurate satellite reflections appear, and structural refinements in superspace reveal a monoclinic modulated phase I2/c(0σ1σ2)0s combining displacements of both K and Nb cations with additional octahedral tilts. Soft modes associated with the tilt instability and the incommensurate modulation are clearly observed in Raman spectra, alongside persistent order-disorder signatures consistent with the known character of $KNbO_3$. SHG measurements confirm that the incommensurate phase remains centrosymmetric, indicating that the re-emergent polar instability does not lead to a macroscopically ferroelectric state but is instead frustrated by competition with the tilt instability. This work provides direct experimental evidence for the theoretically predicted high-pressure polar instability in a lead-free perovskite and highlights the role of order-disorder character and tolerance factor in enabling such a coexistence of competing structural instabilities.