

A pressure induced ferroelectric instability in bulk TiO₂ rutile

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Density functional calculations, within the local density approximation, are used to investigate the isotropic pressure dependence of the geometry and Γ -point phonons of TiO₂ rutile over the range $[-8.6, 8.6]$ GPa. The TO A_{2u} mode, which is the c -axis ferroelectric mode, vanishes at $P \sim -4$ GPa, thereby leading to a crystal instability and a possible ferroelectric phase-transition. Based on this result it is suggested that expanded rutile structures might be created with enhanced dielectric properties by, for instance, thin film growth on a substrate with a small lattice mismatch. A similar behaviour is observed with respect to the analogous mode in the a - b plane (i.e., the softest E_u mode). However, this frequency vanishes at much larger negative pressures (between -15 and -17.5 GPa). The Raman-active B_{1g} mode unusually softens as the pressure increases, and the atomistic origin of this behaviour is explained. The mode softening combined with an orthorhombic distortion causes an instability of the rutile lattice at a critical pressure of 13 GPa. If the rutile phase exists up to such a pressure, this instability will produce a second-order phase transition to a CaCl₂-type structure. The results for the pressure dependence of the geometry and lattice dynamics agree well with the available measured data.