The structural and vibrational properties of selected $BiFeO_3$ polymorphs under pressure: a first principles study

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We analyzed the effect of hydrostatic pressure from 0 GPa to 10 GPa on the phase stability, structural, vibrational, and ferroelectric properties of different bismuth ferrite ($BiFeO_3$ or BFO) polymorphs in the framework of density functional theory. Our work is motivated by numerous experimental studies of the high-pressure behavior of BFO [1-5]. There is a consensus that above 10 GPa BFO transforms to an orthorhombic *Pnma* phase, but there is a dispute regarding the crystal structure of BFO in the range of 4 – 10 GPa. We found that at 0 GPa, the rhombohedral $R3c$ and polar orthorhombic $Pna2_1$ phases are dynamically stable, whereas the orthorhombic nonpolar *Pnma* phase exhibits soft modes. The phonon calculations have shown that the rhombohedral phase is dynamically stable in the entire considered pressure range. At 4 GPa, the Pnma phase became dynamically stable, and its enthalpy became lower compared to the rhombohedral $R3c$ phase. The structural optimization of the $Pna2_1$ phase leads to the slightly distorted version of the *Pnma* phase above 4 GPa. Comparison with the available experimental data suggests that the $Pna2_1$ phase might be the high-pressure phase of $BiFeO_3$.

References:

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