## MS15-P12 | Antiferroelectric Pnma phase: The Missing Element to understand Morphotropic Phase Boundary lead-free $Na_{1/2}Bi_{1/2}TiO_3$ based piezoceramics

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$Na_{1/2}Bi_{1/2}TiO_3$ (NBT) perovskite ($ABO_3$) are of interest due to their role as an end member of lead-free substitutes to replace the commercially dominant $PbZr_{1-x}Ti_xO_3$. NBT exhibits two phase transitions with decreasing temperature: from *Pm*-3*m* to *P*4*bm* and then *R*3*c/Cc*. With pressure, NBT is found to transform from *R*3*c/Cc* phase to *Pnma.* Here, we report high-pressure neutron diffraction combined with density functional perturbation theory (DFT) calculations on $(Na_{1/2}Bi_{1/2}TiO_3)_{0.93}$-$(BaTiO_3)_{0.05}$-$(K_{0.5}Na_{0.5}NbO_3)_{0.02}$ which was chosen as i) it shows the *P*4*bm* structure at ambient temperature and ii) it exhibits optimal piezoelectric properties with a morphotropic phase boundary between *P*4*bm* and *R*3*c* phases.

The calculated full phonon dispersion relations obtained at the GGA level on a model $Na_{1/2}Bi_{1/2}TiO_3$ compound clearly show three instabilities and support a *P*1 triclinic ground state structure. With pressure, the tetragonal phase first transforms to *R*-3*c* at 2 GPa and then to antiferroelectric (AFE) ordered *Pnma* form close to 5 GPa. Large atomic displacement parameters (ADPs) for *A*-site perovskite atoms in the tetragonal phase are definitely associated to the high-pressure AFE symmetry whereas strong ADPs in the *R*-3*c* phase linked to density functional based calculations suggest a weakly polar *P*1 phase. The existence of this AFE state permits to understand disagreements about the average structure and, based on group theory, validates the phase transition sequence in *P-T* space.