Prediction of a Stable Post-Post-Perovskite Structure from First Principles

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ABX₃ perovskites (Pv) form an important class of crystal structures for which A and B are cations and X is typically the oxygen or fluorine anion. Perovskites display a wealth of piezoelectricity. phenomena, such as ferroelectricity, magnetism, multiferroicity, magnetoelectricity, charge and orbital orderings, superconductivity, etc.... As a result, they constitute a rich playground for research and are important for various technologies, which explains the flurry of activities that have been devoted to them. Interestingly, recent works have shown that applying a hydrostatic pressure in some ABX₃ materials can result in the transformation from the Pv structure to the so-called "post-perovskite" (pPv) structure, which can have important physical consequences [1-3]. For instance, the pPv structure discovered in MgSiO₃ explains the existence of anisotropic features in the D" layer of Earth. Moreover, CaRhO3 was recently found to adopt a polymorph that was described as being an intermediate phase between perovskite and post-perovskite [4]. Based on these discoveries as well as recent findings of new high-pressure phases in ABO₃ and ABF₃ systems [5], one may wonder if there is another crystal structure for which Pv or pPv materials can evolve to under hydrostatic pressure. As demonstrated in Ref. [6] and as detailed here, the answer is positive.

More precisely, in this work, a novel stable crystallographic structure is discovered in a variety of ABO₃, ABF₃ and A₂O₃ compounds, via the use of first principles (VASP+USPEX [7]). This novel structure appears under hydrostatic pressure, and can be considered to be a post-post-perovskite (ppPv) phase. It provides a successful solution to experimental puzzles in important systems, and is characterized by one-dimensional chains linked by group of two via edge-sharing oxygen/fuorine octahedra. Such organization automatically results in anisotropic elastic properties and new magnetic arrangements. Depending on the system of choice, this post-post-perovskite structure also possesses electronic band gaps ranging from zero to about 10 eV being direct or indirect in nature, which emphasizes its potential to have striking, e.g., electrical or transport phenomena.

We hope that our work can encourage researchers to confirm the predictions presently reported and to determine properties associated with such novel crystal structure.



FIG. 1. Pressure range of stability of the Pv, pPv and ppPv phases in the ABX₃ and A_2O_3 materials under study. Panels (a) and (b) report materials possessing or missing, respectively, the presently discovered ppPv structure for pressure up to 120 GPa.



FIG. 2. Pressure dependence of the enthalpy of the Pv, pPv and ppPv phases of NaMgF₃ (Panel (a)), along with the schematization of (b) the Pv, (c) pPv and (c) and (d) ppPv crystallographic structures. Note that the enthalpy of the Pv phase has been set to be zero for any pressure in Panel (a), and that the inset of Fig. 2a displays the behavior of the volume versus pressure in the Pv, pPv and ppPv phases.

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