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

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Abstract

A novel stable crystallographic structure is discovered in a variety of $\text{ABO}_3$, $\text{ABF}_3$ and $\text{A}_2\text{O}_3$ compounds (including materials of geological relevance, prototypes of multiferroics, exhibiting strong spin-orbit effects, etc...), via the use of first principles. This novel structure appears under hydrostatic pressure, and is the first “post-post-perovskite” phase to be found. 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/fluorine octahedra. Such unprecedented 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 $\simeq 10$ eV being direct or indirect in nature, which emphasizes its “universality” and its potential to have striking, e.g., electrical or transport phenomena.

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ABX$_3$ 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 phenomena, such as ferroelectricity, magnetism, multiferroicity, piezoelectricity, magneto-electricity, 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 [1]. Interestingly, recent works have shown that applying a hydrostatic pressure in some ABX$_3$ materials can result in the transformation from the Pv structure to the so-called “post-perovskite” (pPv) structure which can have important physical consequences [2–9]. For instance, the pPv structure discovered in MgSiO$_3$ explains the existence of anisotropic features in the D” layer of Earth [8–10]. Moreover, CaRhO$_3$ was recently found to adopt a polymorph that was described as being an intermediate phase between perovskite and post-perovskite [11]. Based on these discoveries, one may wonder if there is another crystal structure (to be termed as “post-post-perovskite” (ppPv)) for which Pv or pPv materials can evolve to under hydrostatic pressure. Positively answering such question will deepen the current knowledge of crystallography and high pressure. Moreover, if such structure does exist, one may also wonder about its structural characteristics and if they can lead to novel physical properties – which is obviously interesting for fundamental reason but also for the design of original devices. It is also of high importance to determine what precise compounds may possess such hypothetical structure. In particular, could it be that such structure is not only the answer to some experimental puzzles in some compounds that are of high geological relevance [2, 3] but can also exist in a variety of materials (ranging from metals to insulators, via multiferroics and systems possessing strong-spin-orbit effects or rare-earth ions)? If that is the case, this structure is “universal” and has the high potential to lead to the discovery of many striking phenomena.

The goal of this Letter is to address all these aforementioned unknown questions, via the use of first-principles calculations. As we will see, surprises are in store since we, e.g., (1) predict that many and various ABX$_3$ and A$_2$O$_3$ materials can transform to a common, novel and stable ppPv structure under hydrostatic pressure; and (2) reveal its unusual structural, magnetic and electronic properties. Moreover, this ppPv structure is likely the “mysterious” phase that has been observed in Refs. [2, 3].

As detailed in the Supplementary Materials (SM), first-principles calculations are performed on many ABX$_3$ and A$_2$O$_3$ materials, with different A and B atoms and with X =
Crystal structures. Let us first concentrate on a specific material that has been experimentally explored under pressure, namely NaMgF$_3$. Figure 2(a) shows that the orthorhombic Pv $Pnma$ phase ($Pv$-$Pnma$) is predicted to be its ground state up to $\simeq 20$ GPa, as consistent with measurements [2, 3, 12]. Such phase is common to many perovskites [13] and is schematized in Fig. 2(b). In this phase, any fluorine (or oxygen) octahedra share corners with their neighboring octahedra along the pseudo-cubic [100], [010] and [001] directions. Figure 2(a) further reveals that NaMgF$_3$ is predicted to experience a phase transition to the (orthorhombic) post-perovskite $Cmcm$ phase ($pPv$-$Cmcm$) at $\simeq 20$ GPa, for which not only the space group but also the crystallographic structure change, as schematized in Fig. 2(c). Interestingly, the $Pv$-$Pnma$–to–$pPv$-$Cmcm$ transition has been observed to occur for pressure around 27-30 GPa and under laser heating (likely, to overcome the kinetic barrier inherent to first-order transitions) [2, 3] in NaMgF$_3$, which is rather consistent with our prediction of a corresponding critical pressure of $\simeq 20$ GPa at 0 Kelvin. As indicated by Fig. 2 and Table I of the SM, the $pPv$-$Cmcm$ phase differs from the $Pv$-$Pnma$ structure by the existence of two-dimensional sheets formed by octahedra that share edges along the $a$-axis and corners along the $c$-axis. These two-dimensional sheets are stacked along the $b$-axis with an interlayer made of $A$ atoms separating any two neighboring sheets. As a result, the elastic (stiffness) constant of $pPv$-$Cmcm$ is much lower along the $b$-axis than along the $a$ or $c$ axis for any material, including NaMgF$_3$ (see Table II of the SM) and MgSiO$_3$ – which, for this latter compound, is consistent with the seismic anisotropy observed in the so-called D” layer of Earth [8, 10].

As also revealed by Fig. 2(a), we further found that NaMgF$_3$ undergoes another transition at $\simeq 51$ GPa, for which the space group and crystallographic structure both change again: the resulting phase re-adopts the $Pnma$ space group but within a different crystallographic structure that is termed “post-post-perovskite” [3, 14, 15] and that is denoted as $ppPv$-$Pnma$ in the following. Its structural characteristics are shown in Figs. 2(d) and 2(e). Interestingly, while $ppPv$-$Pnma$ has never been previously reported in any material, its present discovery solves a puzzle: it likely is the so-called mysterious “N-phase” that has been observed in Ref.[2, 3], based on the facts that (i) it experimentally appears as a result of a phase transformation from the $pPv$-$Cmcm$ phase at 56 GPa under laser-heating of about 2000 K (as consistent with our predicted $pPv$-$Cmcm$–to–$ppPv$-$Pnma$ transition for a
critical pressure $\simeq 51$ GPa at $T = 0$ K); (ii) the “N-phase” has been assigned an orthorhombic symmetry [2], in line with the $Pnma$ space group we presently found for our ppPv structure [16]; and (iii) our simulated X-Ray Diffraction pattern of ppPv-$Pnma$ is consistent with the one experimentally found in Ref.[3] for this N-phase (see Fig. 3 of the SM).

Remarkably, comparing Figs. 2(c) with 2(d) and 2(e) reveals that the transformation from pPv-$Cmcm$ to ppPv-$Pnma$ results in the breaking of the two-dimensional octahedra sheet at the shared corners in favor of one-dimensional chains that are elongated along the $b$-axis of the ppPv-$Pnma$ structure. These chains organize themselves by group of two (with the two chains forming the double chain being parallel to each other along the $b$-axis), as a result of edge-sharing octahedra. As shown in Table I of the SM, for a given pressure of 60 GPa (which is rather close to the predicted pPv-$Cmcm$–to–ppPv-$Pnma$ transition), the formation of these double chains leads, in NaMgF$_3$, to the $b$ and $c$ lattice constants of ppPv-$Pnma$ increasing by 4.3% and 25.3%, respectively, with respect to the $a$ and $b$ lattice constants of pPv-$Cmcm$. On the other hand, the $a$ lattice parameter of ppPv-$Pnma$ decreases by 24.9% with respect to the $c$ lattice constant of pPv-$Cmcm$ (note that the $b$-axis is parallel to the chains in ppPv-$Pnma$ while it is perpendicular to the octahedra sheets in pPv-$Cmcm$, implying that comparisons have to be made between the $(a,b,c)$ triad axis of ppPv-$Pnma$ and the $(c,a,b)$ triad axis of pPv-$Cmcm$). Such changes in lattice constants result in a decrease of 1.84% of the volume at the pPv-$Cmcm$–to–ppPv-$Pnma$ transition in NaMgF$_3$, which is a prediction that can be easily checked by measurements. Note also that the octahedra are more distorted in ppPv-$Pnma$ than in pPv-$Cmcm$, as evidenced by the facts that the six Mg-F bonds of the octahedra in ppPv-$Pnma$ adopt four different values equal to 1.813 Å, 1.871 Å (doubly degenerate), 1.888 Å (doubly degenerate) and 1.942 Å, respectively, while those of pPv-$Cmcm$ only split between two values of 1.785 Å (doubly degenerate) and 1.846 Å (four times degenerate), respectively, for a pressure of 60 GPa. The fluorine octahedra therefore become 0.84% larger in ppPv-$Pnma$ than in pPv-$Cmcm$ (even if the volume decreases), as edge-sharing allows for more compact packing. Moreover, in the ppPv-$Pnma$ phase, any Mg ion belonging to one chain gets rather close to a specific F ion belonging to the adjacent chain (indicated by the dashed line in Fig. 2(d)) forming the double chains and therefore leads to an increase in coordination number from 6 to “6+1”. For instance, at 60 GPa, the bond between these Mg and specific F ions is about 2.103 Å, which is comparable to the distances of 1.813 Å–1.942 Å between Mg and F ions belonging
Figure 1(a) also shows that many materials are also predicted to exhibit the aforementioned Pv-Pnma–to–pPv-Cmcm and pPv-Cmcm–to–ppPv-Pnma transitions, but at different critical pressures. On the other hand, Fig. 1(a) further indicates that some materials are predicted to directly transform from Pv-Pnma to ppPv-Pnma without adopting the intermediate pPv-Cmcm phase, as the pressure increases. Examples include (i) two prototypes of multiferroic materials, BiFeO$_3$ and BiCrO$_3$ [18, 19]; (ii) CaMnO$_3$ that has been predicted to exhibit both magnetic and electric orderings when grown as a strained film [20, 21]; and (iii) the rare-earth ferrites RFeO$_3$ [22–24] with small or intermediate ionic radius. For instance, GdFeO$_3$ directly undergoes a transition from Pv-Pnma to ppPv-Pnma at the pressure of $\simeq 56.5$ GPa. Conversely, there are some materials, such as CaBO$_3$ with $B = \text{Ru, Ir, Rh, Pt}$ (that have been investigated because of their analogy with MgSiO$_3$ [4–7, 25, 26] or because of the strong effect of spin orbit interactions on some of their physical properties [27]) that do not exhibit the Pv-Pnma phase but rather evolve from pPv-Cmcm to ppPv-Pnma, as a hydrostatic pressure is applied and increased. In particular, we predict that the ppPv-Pnma phase of CaRuO$_3$ will appear at a pressure of 33.8 GPa, which should make its observation rather easily feasible. On the other hand and as shown in Fig. 1(b), no ppPv structure was found up to 120 GPa in some other systems, such as RFeO$_3$ compounds with large ionic radius (i.e., $R = \text{Nd, Pr, Ce and La}$), MgSiO$_3$, Mn$_2$O$_3$ or Al$_2$O$_3$ – as consistent with measurements and previous computations [8, 9, 28–30] (note that the SM provides a more detailed comparison between our predictions and these previous works).

*Dynamical stability.* The ppPv-Pnma structure is dynamically stable in its pressure range of stability for all the materials shown in Fig. 1(a). Two examples are shown in Figs. 1(a) and 1(c) of the SM for NaMgF$_3$ and GdFeO$_3$, respectively, both under a pressure of 60 GPa. In fact, we also numerically found that, in several studied compounds, ppPv-Pnma does not have any unstable phonon even in pressure regions for which this phase is not the lowest one in enthalpy. For instance, ppPv-Pnma is dynamically stable even at zero pressure in, e.g., CaPtO$_3$, which likely implies that this phase can be quenched to ambient pressure in this material (especially because the difference in enthalpy between pPv-Cmcm and ppPv-Pnma is found to be as small as 181 meV/5-atom at zero pressure in CaPtO$_3$). Conversely, other phases, such as pPv-Cmcm, can also have no unstable phonon in the pressure range for which ppPv-Pnma has the lowest enthalpy, which implies that (i) pPv-Cmcm may still be
experimentally found in some materials at pressure higher than the predicted pPv-Cmcm--ppPv-Pnma transition pressure and (ii) observing ppPv-Pnma phase in these materials may require the use of laser heating (to overcome kinetic barrier).

Electronic structure. We also numerically found that, within ppPv-Pnma, the electronic band gap can be rather quantitatively different between investigated materials (see Table III and Fig. 1 of the SM). For instance, the calculated band gap of NaMgF$_3$ is as large as 9.04 eV for a pressure of 60 GPa while it is dramatically reduced to 0.83 eV for GdFeO$_3$ under the same pressure. In fact, a few systems are even metallic above the pressure at which the ppPv-Pnma phase begins to appear. Examples include CaRhO$_3$ at 70 GPa and CaIrO$_3$ at 90 GPa. Equally striking and as shown in Fig. 1 of the SM too, even the character of the band gap (that is direct versus indirect) can be altered when going from one material to another within ppPv-Pnma. Such electronic flexibility may result, in the future, to the discovery of anomalous properties (such as metal-insulator transitions [31]) or highly-desired features (such as a direct-band gap in the frequency spectrum needed for photovoltaic devices [32] or light-emitting devices [33]) in materials possessing the ppPv-Pnma structure.

Magnetic ordering. Interestingly, some ABO$_3$ materials, that are predicted to exhibit ppPv-Pnma structure, possess A and/or B atoms that are magnetic. As a result, novel or striking magnetic arrangements should emerge, especially when recalling that ppPv-Pnma adopts unusual “double” one-dimensional chains inside which A and B bond with O atoms (see Figs. 2(d) and 2(e)). Let us, for instance, consider the case of the ppPv-Pnma phase of GdFeO$_3$ at 60 GPa and include the 4f electrons of Gd in the valence in the calculations, thus allowing both Gd and Fe ions to adopt localized magnetic moments (that are found to be 6.90 $\mu_B$ and 4.12 $\mu_B$, respectively). Practically, enthalpies of different collinear magnetic configurations are computed and used to extract the coupling coefficients ($J_{BB,chain}$, $J_{BB,across}$, $J_{BA,single}$, $J_{BA,four}$) of the model described by $H = \frac{1}{2}J_{BB,chain}\sum_{i,j}S_i\cdot S_j + \frac{1}{2}J_{BB,across}\sum_{i,j}S_i\cdot S_j + \frac{1}{2}J_{BA,single}\sum_{i,j}S_i\cdot S_j + \frac{1}{2}J_{BA,four}\sum_{i,j}S_i\cdot S_j$, where the sums over $i$ run over all Fe atoms while the first (respectively, last) two sums over $j$ run over specific Fe (respectively Gd) atoms that will be indicated below. As depicted in Fig. 3, the strongest coupling coefficient (denoted by $J_{BB,chain}$) is found to be 2.86 meV (that is antiferromagnetic in nature) and is between Fe ions that are distant (by $\simeq 3.02$ Å) along the $b$-axis. Interestingly, the coupling between Fe ions that belong to two adjacent and parallel one-dimensional chains (and are distant by $\simeq 2.67$ Å) is also antiferromagnetic in nature but is of smaller
magnitude since it is equal to 1.52 meV (this parameter is denoted here as $J_{BB,\text{across}}$). As a result and as shown in Fig. 3(a), the magnetic ground state of GdFeO$_3$ possesses one-dimensional antiferromagnetic chains elongating along the $b$-axis and formed by Fe ions with each of these Fe ions having two neighboring Fe ions of opposite spins and that belong to the adjacent parallel chain. Note that the particular triangular-like geometry seen by any magnetic $B$ ion (see Fig. 3(a)) because of the formation of the double one-dimensional chains inherent to ppPv-$Pnma$ in $ABO_3$ materials is a perfect “recipe” to generate the so-called geometric frustration [34, 35] in the specific (and presently hypothetical) case that $J_{BB,\text{chain}}$ and $J_{BB,\text{across}}$ would still be antiferromagnetic in nature but would now be close to each other in magnitude (unlike in GdFeO$_3$). Searching for such compounds or the hypothetical pressure giving rise to such condition in some materials therefore constitutes a promising avenue to pursue in the future. Note also that we numerically found that, in the ppPv-$Pnma$ phase of GdFeO$_3$ at 60 GPa, magnetic interactions between Gd ions are negligible (as consistent with the deep $f$-shell of Gadolinium) but Fe ions are antiferromagnetically coupled with their closest Gd ions. As indicated in Fig. 3(b), the resulting coupling is $J_{BA,\text{single}} = 1.22$ meV between Fe and Gd ions that form single bond (and are distant by 2.783 Å) while it is $J_{BA,\text{four}} = 0.73$ meV between Fe and Gd ions that are tetrahedrally bonded (and distant by 3.121 Å). As a result, the magnetic ordering of Gd ions is governed by their interaction with Fe ions and is the one depicted in Fig. 3(b).

In summary, we used first-principles techniques to discover a common and stable ppPv crystal structure in a variety of $ABX_3$ and $A_2O_3$ materials under pressure. Such phase exhibits one-dimensional structural characteristics which naturally lead to strong anisotropy and emergence of novel magnetic orderings, and provides a plausible explanation for the mysterious phase that has been reported in Refs. [2, 3]. Moreover, the electronic band gap of this phase is highly dependent on the system and can be of rather different nature and magnitude, which points towards the “universal” aspect of this new phase. We hope that this Letter will encourage researchers to confirm the predictions presently reported and to determine properties associated with such novel crystal structure.

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FIG. 1: (Color online). Pressure range of stability of the P\textit{v}-\textit{Pnma}, \textit{pPv-Cmcm} and \textit{ppPv-Pnma} phases in the \textit{ABX}_3 and \textit{A}_2\textit{O}_3 materials under study. Panels (a) and (b) report materials possessing or missing, respectively, the presently discovered \textit{ppPv-Pnma} structure for pressure up to 120 GPa.

FIG. 2: (Color online). Pressure dependence of the enthalpy of the P\textit{v}-\textit{Pnma}, \textit{pPv-Cmcm} and \textit{ppPv-Pnma} phases of NaMgF\textsubscript{3} (Panel (a)), along with the schematization of (b) the P\textit{v}-\textit{Pnma}, (c) \textit{pPv-Cmcm} and (c) and (d) \textit{ppPv-Pnma} crystallographic structures. Note that the enthalpy of the P\textit{v}-\textit{Pnma} phase has been set to be zero for any pressure in Panel (a).
FIG. 3: (Color online). Magnetic ground state of the ppPv-\textit{Pnma} phase of GdFeO$_3$ under 60 GPa. Panel (a) reports the strength of the magnetic interactions and the resulting magnetic ordering between Fe ions, while Panel (b) depicts the coupling coefficients associated with Fe and Gd magnetic interactions as well as the spin pattern adopted by these two types of ions.
Supplemental Material for
“Prediction of a Stable Post-Post-Perovskite Structure from First Principles”

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The goal of this Supplementary material (SM) is to provide details about the methods used, as well as additional information.

**Methods:**

Chronologically, this study started by applying the *ab-initio* evolutionary algorithm USPEX [1–4] to LuFeO$_3$. Calculations of (LuFeO$_3$)$_n$ with 10, 20 and 30-atom cells (corresponding to $n = 2, 4$ and $6$, respectively) were performed at 60 GPa and 100 GPa. We successfully reproduced the occurrence of the Pv-$Pnma$ phase of LuFeO$_3$, which is often referred to as the GdFeO$_3$-type structure and is known to be present in many perovskites [5]. We further predicted the existence of two other stable crystallographic structures of low enthalpy, viz. pPv-$Cmcm$ and ppPv-$Pnma$, in LuFeO$_3$. Then, the various $ABX_3$ and $A_2O_3$ materials indicated in Fig. 1 of the manuscript were systematically studied under hydrostatic pressure, using the Vienna *ab-initio* simulation package (VASP) [6]. Technically, the generalized gradient approximation (GGA), altogether with the PBE functional for solid (PBE$_{sol}$) [7], were employed since they are known to yield accurate structural parameters [8]. Local density approximation (LDA) was also tested for NaMgF$_3$, yielding transition pressures merely a few GPa smaller than those from GGA. The projector augmented wave (PAW) method [9] was used to mimic electron-ion interactions with an energy cutoff of 500 eV for all the studied compounds. Hydrostatic pressure was typically simulated up to 120 GPa. 20-atom unit cells were typically adopted for the three investigated structures (i.e., Pv-$Pnma$, pPv-$Cmcm$, ppPv-$Pnma$), with $\Gamma$-centered $6\times6\times4$, $8\times4\times6$ and $6\times8\times4$ $k$-point meshes, respectively. Note, however, that 40-atom cells with a doubled $b$ lattice parameter have also been employed when studying the collinear magnetic properties of the ppPv-$Pnma$ phase of GdFeO$_3$ depicted in Fig. 3 of the manuscript. In that case, the $\Gamma$-centered $6\times6\times4$ $k$-point mesh was used and the $f$ electrons were included in valence to investigate the contribution of Gd to the magnetic properties. All the studied structures were fully relaxed during the simulations. For instance, the Hellman-Feynman forces were systematically smaller than 0.001 eV/Å when using 20-atom unit cells, which then allowed to compute elastic constants in VASP (using an atomic displacement of 0.015 Å and each step being converged to $10^{-8}$ eV). For all the investigated compounds having the ppPv-$Pnma$ structure (see Fig. 1 of the manuscript), the phonon spectra were calculated using the PHONOPY software [10]. In that case, a $2\times3\times1$ supercell with 120 atoms was employed to compute the force constants, and the $\Gamma$ point was used to sample the Brillouin zone (the validity of such $k$-point sampling
was checked by testing $4 \times 4 \times 4 \Gamma$-centered $k$-point mesh). The energy was converged to $10^{-8}$ eV. Other technical details include (i) the typical treatment of 4f electrons in the core (except for the results of Fig. 3 of the manuscript) if the $A$ ion of the $ABO_3$ material is a rare-earth ion, based on our calculation results showing that freezing such electrons in the core versus considering them inside the valence only results in a 0.5% underestimation of the lattice constants for the ppPv-$Pnma$ phase of GdFeO$_3$; and (ii) the use of an effective Hubbard U parameter when ions possess localized $d$ electrons. Typically, we employ $U = 4$ eV for the $3d$ electrons of Ti, Cr, Mn, Fe and Co [8, 11], and $U = 2.8$ eV for the $4d$ electrons of Rh, Ru as well as for the $5d$ electrons of Ir and Pt [12]. Note that we also tested $U = 0$ eV, 4 eV and 5.3 eV for CaMnO$_3$. These tests show that varying the Hubbard U parameter only makes a difference in the lattice constants of the order of 0.5% for the ppPv-$Pnma$ phase and has no qualitative influence on the phase diagram (transition pressures were only found to shift by a few GPa).

*Crystallographic structure and elastic constants:*

In Table I we report an example of crystallographic structures associated with Pv-$Pnma$, pPv-$C'mcm$ and ppPv-$Pnma$ phases. Such data can be used by computational scientists to, e.g., calculate properties of our newly discovered ppPv-$Pnma$ structure or by experimentalists to, e.g., check if X-ray or neutron patterns (they obtained or will obtain) can be well fitted by one of these three phases.

Table II shows a specific hierarchy between elastic constants, such as the facts that $C_{11}$ is much smaller than $C_{22}$ and $C_{33}$ in the Pv-$Pnma$ phase while it is $C_{22}$ that is the smallest (respectively, largest) among the $C_{ii}$ coefficient in pPv-$C'mcm$ (respectively, ppPv-$Pnma$) – as consistent with their crystallographic structures. Such information can be useful to, e.g., earth-scientists since it has connection with seismic anisotropy [13, 14].

*Phonon spectra and electronic structures:*

Figure 1 of this SM shows the phonon spectra and electronic band structures of the ppPv-$Pnma$ phase for NaMgF$_3$ and GdFeO$_3$ under 60 GPa, to demonstrate the stability of this phase as well as the fact that the electronic band gap can have different magnitude and nature (i.e., direct versus indirect) for different materials adopting this ppPv-$Pnma$ phase.

Table III is also reported here to emphasize that the presently discovered ppPv-$Pnma$ structure can have a wide range of electronic band-gap, implying that the systems adopting it can either be metallic, semiconductor or strong insulator – which may broaden their possible
range of technological application (especially, if the ppPv-Pnma phase can be quenched to ambient conditions).

*Phase diagram of rare-earth ferrites:*

Furthermore, Fig. 2 of the SM displays the phase diagram of the rare-earth ferrites (RFeO$_3$) materials revealing the dependence of transition pressure with rare-earth ionic radius. This is done in order to potentially guide experimentalists in their search of pPv-Cmcm and ppPv-Pnma states in these compounds, as well as to illustrate that their properties do depend on the size of R ion -- as already known for other quantities [15–17].

*Comparison between our predictions and previous works:*

1) *For NaMgF$_3$:*

Figure 3 of this SM provides our predicted X-Ray Diffraction (XRD) pattern for the Pv-Pnma, pPv-Cmcm and ppPv-Pnma phases of NaMgF$_3$ at 55 GPa, assuming that the incident X-ray has a wavelength of 0.3344 Å. This particular wavelength was chosen because it is the one experimentally used in Refs. [18, 19]. Our predicted XRD spectra for the pPv-Cmcm phase agrees rather well with the corresponding experimental one (for the post-perovskite structure) shown in the inset of Fig. 3 of Ref. [19] for NaMgF$_3$ under a hydrostatic pressure of 55 GPa, which further attests the accuracy of the simulations. Such agreement is further emphasized in Table IV that reports the the calculated and experimental peak positions of the pPv-Cmcm phase at 55 GPa.

Regarding the comparison between our simulations for the XRD pattern of the ppPv-Pnma phase and the XRD pattern of the N-phase of NaMgF$_3$ measured at 55 GPa after laser heating (which is shown in the inset of Fig. 3 in Ref. [19]), one first has to know that our predicted XRD of the ppPv-Pnma corresponds to a $\simeq 2.3\%$ increase of the lattice constants with respect to those predicted by our 0 K first-principles calculations. This increase was done in order to have the same volume than in the measurements, and may reflect thermal expansion (since a high temperature of $\sim 2000$ K was experimentally found necessary for the N-phase to emerge, likely due to kinetic reason) or some inaccuracy in the calculations. Interestingly, such increase does not qualitatively affect the XRD pattern but was rather found to “only” shift the XRD peaks by small amounts. Such small shifts lead to a rather good agreement between the position of many of our simulated peaks and the position of the experimental peaks that were believed to originate from the N-phase in Ref. [19] -- as evidenced in Fig. 3(c) of this SM and in Table IV. Such agreement is a
strong evidence that the experimentally observed N-phase of Refs. [18, 19] is our predicted ppPv-Pnma phase. Interestingly, Figure 3 and Table IV of this SM also provide additional information. For instance, it suggests that the rather weak peak at 4.5° that was believed to be due to the N-phase in Ref. [19] can in fact originate from the pPv-Cmcm state – since one can see such peak in Fig. 3(b) but not in Fig. 3(c) of this SM. Similarly, Ref. [19] assumed that the series of peak they found in the 7° - 7.5°, 9.5° - 10° and 12.8° - 14° ranges of angle are caused by the post-perovskite pPv-Cmcm phase, while these peaks also exist in the post-post-perovskite phase (they are the peaks that do not possess corresponding arrows in Fig. 3(c) of this SM).

2) For NaZnF₃:

Figure 1(a) of the manuscript shows that our calculations yield, in the NaZnF₃ compound, (i) a transition from Pv-Pnma to pPv-Cmcm at 8.1 GPa, as rather consistent with the recent measurement of Ref.[20] yielding the same transition at around 14 GPa; and (ii) a transition from pPv-Cmcm to ppPv-Pnma at 20.3 GPa, which suggests that the unidentified phase that has been observed to coexist with pPv-Cmcm for pressure above 25 GPa in NaZnF₃ [20] may be our presently predicted ppPv-Pnma. Such hint is strengthened when realizing that Ref.[20] reported a large elastic anisotropy in NaZnF₃ above 25 GPa, which is consistent with our numerical finding that the elastic (stiffness) constant in the ppPv-Pnnm phase of any material should be larger along the b-axis than along the a or c axis due to the fact that this b-axis is precisely the direction of elongation of the one-dimensional chains (see Table II of the SM for NaMgF₃). However, the comparison between our predicted XRD spectra of ppPv-Pnma for NaZnF₃ shown in Fig. 4(c) of this SM (for a pressure of 30 GPa and an incident wavelength of 0.3738 Å) and the experimental XRD pattern depicted in Fig. 2 of Ref. [20] can not allow us to fully guarantee that the unidentified phase of Ref. [20] is our discovered ppPv-Pnnm phase. This is because it is difficult to know what are the peaks solely due to this unidentified phase in the pattern shown in Fig. 2 of Ref. [20] (as a result of the coexistence between different phases). However, it is promising to realize that our simulated XRD spectra of ppPv-Pnma (see Fig. 4(c) of this SM) possesses a relatively strong peak for an angle of around 5.5°, and as observed in Ref. [20], such latter peak is inconsistent with the pPv-Cmcm state but is rather associated with this unidentified phase. We thus hope that the simulated XRD presented in Fig. 4(c) will soon allow the definite experimental identification of this latter phase found in Ref. [20].
3) For MgSiO$_3$:

Figure 1(b) of the manuscript shows that ppPv-$Pnma$ is not predicted to form in MgSiO$_3$ when the pressure is applied up to 120 GPa (note that we also conducted further calculations up to 400 GPa in this specific material, and still did not found this ppPv-$Pnma$ phase). In this important material present in the lower earth mantle, only a single Pv-$Pnma$–to–pPv-$Cmcm$ transition is found at 95.5 GPa, which is in reasonable agreement with the known experimental value of $\approx$ 125 GPa happening at high temperature [21] and with previous first-principles calculations yielding 83.7 GPa or 98.7 GPa for the critical pressure [13] of that precise transition.

4) For Mn$_2$O$_3$:

Mn$_2$O$_3$ is also predicted to undergo the single Pv-$Pnma$–to–pPv-$Cmcm$ transition, but at a smaller pressure of 25.3 GPa – which agrees rather well with the experimental data of Ref.[22] reporting a critical pressure being in the 27-36 GPa range at room temperature.

5) For Al$_2$O$_3$:

It is also worthwhile to realize that our calculations yield a Pv-$Pnma$–to–pPv-$Cmcm$ transition in Al$_2$O$_3$ for a pressure of 95.5 GPa, which slightly underestimates the critical pressure of 130 GPa at which the pPv-$Cmcm$ is known to occur in this compound [23, 24].

Discussion about other phases and decomposition

This latter underestimation between the theoretical and experimental pressures at which pPv-$Cmcm$ forms in Al$_2$O$_3$ is likely due to the fact that, experimentally, the phase adopted by Al$_2$O$_3$ before the transition is the so-called Rh$_2$O$_3$(II)-type state rather than the Pv-$Pnma$ phase. Such discrepancy between measurements and our calculations takes its origin from the fact that we exclusively concentrate on three phases here (i.e., Pv-$Pnma$, pPv-$Cmcm$ and ppPv-$Pnma$) for all our investigated compounds – in order to demonstrate their possible stability in a wide range of materials. As a result, some transitions may be missed by the simulations or one of the three investigated states can occur at a different pressure with respect to experiments in a few compounds (namely, those for which neither Pv-$Pnma$ nor pPv-$Cmcm$ and ppPv-$Pnma$ are the most stable state between 0 and 120 GPa). For instance, Fig. 5 of this SM indicates what happens to the phase transitions summarized in Fig. 1 of the manuscript, when the P2$_1$/m phase discovered in CaRhO$_3$[25] is also taken into account in the simulations. In that case, out of the thirty six compounds we investigated, eight exhibit some modifications for their phase diagram: P2$_1$/m appears, in some pressure
range, in-between the Pv-Pnma (respectively, pPv-Cmcm) and ppPv-Pnma structures for ErFeO$_3$ and TmFeO$_3$ (respectively, LuFeO$_3$, CaTiO$_3$, CaRhO$_3$, CaPtO$_3$ and CaIrO$_3$), while it exists from around 86 GPa up to our highest investigated pressure of 120 GPa in InFeO$_3$. It is also interesting to notice that comparing Fig. 3 of Ref. [25] with Figs. 2(c) and 2(d) of the manuscript suggests that this P2$_1$/m phase can be thought as being a structural bridge between the known pPv-Cmcm state and the presently discovered ppPv-Pnma phase, since it possesses edge-sharing and corner-sharing octahedra sheets (as in pPv-Cmcm) but also chains propagating along the $b$-axis (as in ppPv-Pnma).

One should also be aware that some previous first-principles calculations [26, 27] suggested that some ABX$_3$ materials, namely MgSiO$_3$ or NaMgF$_3$, may decompose at high pressure into a AX+BX$_2$ mixture, which can therefore render the observation of some of our phases challenging. However, such proposed decomposition was predicted to arise in MgSiO$_3$ at much higher pressure (namely, above 1000 GPa) than the ones presently investigated and was not experimentally found in NaMgF$_3$ up to 70 GPa [28]. Moreover, it is also important to realize that states that are not ground state can be created and then stabilized in many materials by various techniques if these states are metastable and that a large kinetic barrier separates them with the ground state – as it is the case for ppPv-Pnma (see our discussion about dynamic stability in the manuscript). We are therefore confident that our present results will be soon experimentally confirmed.

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TABLE I: Crystallographic structures of NaMgF$_3$ in the three investigated phases (Pv-Pnma, pPv-Cmcm and ppPv-Pnma), at 60 GPa. Mg-F bond lengths within the octahedra and their degeneracies (indicated in parenthesis) are also given for information.

| Phase          | a          | b          | c          | α = β = γ = 90° |
|----------------|------------|------------|------------|-----------------|
| PV-Pnma        | 5.167 Å    | 6.805 Å    | 4.299 Å    |                 |
| Atom           | Wyc. | x    | y    | z    | Mg-F bond length |
| F              | 8d    | 0.3193 | 0.5644 | 0.6477 |                |
| F              | 4c    | 0.5412 | 0.25  | 0.8673 | 1.807(×2)       |
| Mg             | 4b    | 0      | 0     | 0.5   | 1.832(×2)       |
| Na             | 4c    | 0.8939 | 0.25  | 0.0510 | 1.821(×2)       |
| PV-Cmcm        | 2.713 Å    | 8.154 Å    | 6.766 Å    |                 |
| Atom           | Wyc. | x    | y    | z    | Mg-F bond length |
| F              | 8f    | 0     | 0.64457 | 0.43765 |              |
| F              | 4c    | 0     | -0.06993 | 0.25   | 1.785(×2)       |
| Mg             | 4a    | 0     | 0     | 0     | 1.846(×4)       |
| Na             | 4c    | 0     | 0.25039 | 0.25   |                |
| PP-Pnma        | 5.082 Å    | 2.829 Å    | 10.215 Å    |                 |
| Atom           | Wyc. | x    | y    | z    | Mg-F bond length |
| F              | 4c    | 0.0036 | 0.25  | 0.8980 |                |
| F              | 4c    | 0.1573 | 0.25  | 0.2823 | 1.813           |
| F              | 4c    | 0.8600 | 0.25  | 0.4504 | 1.942           |
| Mg             | 4c    | 0.7739 | 0.25  | 0.0499 | 1.871(×2)       |
| Na             | 4c    | 0.6266 | 0.25  | 0.8007 | 1.888(×2)       |
TABLE II: Elastic constants of NaMgF$_3$ for the three investigated Pv-$Pnma$, pPv-$Cmcm$ and ppPv-$Pnma$ phases, for a hydrostatic pressure of 0 GPa and 60 GPa. These elastic constants are given in GPa units and the ‘1’, ‘2’ and ‘3’ subscripts refer to the a-, b- and c-axis, respectively, of each of these three phases.

|       | Pv-$Pnma$ 0 GPa | Pv-$Pnma$ 60 GPa | pPv-$Cmcm$ 0 GPa | pPv-$Cmcm$ 60 GPa | ppPv-$Pnma$ 0 GPa | ppPv-$Pnma$ 60 GPa |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $C_{11}$ | 137             | 224             | 179             | 431             | 65              | 324             |
| $C_{22}$ | 159             | 477             | 111             | 271             | 163             | 401             |
| $C_{33}$ | 155             | 386             | 170             | 458             | 117             | 358             |
| $C_{44}$ | 49              | 126             | 28              | 104             | 25              | 111             |
| $C_{55}$ | 43              | 81              | 28              | 102             | 36              | 130             |
| $C_{66}$ | 53              | 114             | 38              | 198             | 39              | 210             |
| $C_{12}$ | 58              | 220             | 34              | 226             | 33              | 233             |
| $C_{13}$ | 42              | 197             | 52              | 151             | 46              | 185             |
| $C_{23}$ | 46              | 169             | 27              | 232             | 28              | 207             |
TABLE III: Electronic band gaps of the investigated materials in their ppPv-Pnma phase, just above their transition pressure. The nature of the band gap is indicated inside the parenthesis in the second column. Note that we numerically found (not shown here) that our predicted band gap of BiFeO$_3$ in its $R3c$ ground state is 2.1 eV, while the corresponding experimental value is close to 2.5 eV [29]. Such comparison indicates that, as common with first-principles-calculations, our predicted band gaps in this Table III likely underestimate measurements by around 0.4 eV. Note that we also performed hybrid functional calculations [30] (not shown here) and found that, for BFO systems, they overestimate the band gap by $\simeq 0.8$eV.

| Compounds     | Gap (in eV) | Pressure (in GPa) at which the gap is calculated | Pressure (in GPa) at which ppPv-Pnma appears |
|---------------|-------------|-----------------------------------------------|---------------------------------------------|
| NaCoF$_3$     | 0.21 (direct) | 20                                           | 14.8                                        |
| NaZnF$_3$     | 4.64 (direct) | 30                                           | 20.3                                        |
| NaNiF$_3$     | 3.56 (direct) | 80                                           | 78.7                                        |
| NaMgF$_3$     | 9.04 (direct) | 60                                           | 51.1                                        |
| LuFeO$_3$     | 0.25 (indirect) | 70                              | 64.9                                        |
| LnFeO$_3$     | $\sim 0$ (indirect) | 120                                      | 118                                         |
| CaTiO$_3$     | 1.89 (direct) | 80                                           | 70.8                                        |
| CaCrO$_3$     | 0.42 (direct) | 60                                           | 60                                          |
| MnGeO$_3$     | metallic     | 110                                          | 110                                         |
| Fe$_3$O$_3$   | 0.46 (indirect) | 90                              | 80.7                                        |
| CaMnO$_3$     | 1.25 (indirect) | 30                              | 23.6                                        |
| TmFeO$_3$     | 0.36 (indirect) | 60                              | 54.6                                        |
| ErFeO$_3$     | 0.39 (indirect) | 60                              | 53.8                                        |
| HoFeO$_3$     | 0.38 (indirect) | 60                              | 53.6                                        |
| DyFeO$_3$     | 0.44 (indirect) | 60                              | 53.6                                        |
| TbFeO$_3$     | 0.44 (indirect) | 60                              | 54.4                                        |
| GdFeO$_3$     | 0.83 (indirect) | 60                              | 56.5                                        |
| SmFeO$_3$     | 0.51 (indirect) | 80                              | 71.8                                        |
| PmFeO$_3$     | 0.50 (indirect) | 100                             | 90.7                                        |
| BiCrO$_3$     | $\sim 0$ (indirect) | 60                              | 50.5                                        |
| BiFeO$_3$     | $\sim 0$ (indirect) | 100                             | 98.2                                        |
| CaPtO$_3$     | 1.56 (indirect) | 90                              | 81                                          |
| CaIrO$_3$     | metallic     | 90                                           | 86.5                                        |
| CaRuO$_3$     | 0.54 (direct) | 40                                           | 33.8                                        |
| CaRhO$_3$     | metallic     | 70                                           | 64.5                                        |
TABLE IV: Comparison between the measurements of Ref. [19] and our present simulations for some XRD peak positions (in degrees) of the pPv-Cmcm state and of another phase of NaMgF$_3$ at 55 GPa, for an incident X-ray having a wavelength $\lambda = 0.3344$ Å. This other phase is ppPv-Pnma in the simulations while it is denoted as the N-phase in the experiments of Refs. [18, 19]. Note that the lattice constants are expanded by 2.3% with respect to their predicted 0 K values for the computation of the theoretical XRD pattern of ppPv-Pnma to reproduce the experimental volume of the N-phase. Note also that the experimental peak positions of the N-phase reported in this Table are those believed to originate from this N-phase in Ref. [19], but that other peaks have also been measured in the XRD spectra of Ref. [19] (see our discussion in the SM). The peaks are indexed following the order of increasing $2\theta$ (in Deg.), as indicated in the inset of Fig. 3 of Ref. [19].

| Peak index | pPv-Cmcm pPv-Cmcm | N-phase/ppPv-Pnma N-phase/ppPv-Pnma |
|------------|--------------------|-------------------------------------|
|            | Experiment [19] Theory | Experiment [19] Theory |
| 1          | -                   | 4.6 | 4.5 | - |
| 2          | 5.6                 | 5.6 | 5.0 | 5.1 |
| 3          | 7.2                 | 7.3 | 6.9 | 6.8 |
| 4          | 7.4                 | 7.4 | 7.9 | 8.1 |
| 5          | 7.9                 | 7.9 | 8.0 | 8.3 |
| 6          | 9.6                 | 9.7 | 8.2 | 8.5 |
| 7          | 9.8                 | 9.9 | 8.8 | 9.1 |
| 8          | 10.2                | 10.3| 9.0 | 9.3 |
| 9          | 11.2                | 11.3| 10.2| 10.4|
| 10         | -                   | -   | 10.7| 10.9|
| 11         | -                   | -   | 11.1| 11.2|
| 12         | -                   | -   | 11.4| 11.6|
| 13         | -                   | -   | 11.6| 11.8|
| 14         | -                   | -   | 12.0| 12.2|
| 15         | -                   | -   | 12.6| 12.9|
| 16         | -                   | -   | 14.4| 14.7|
FIG. 1: (Color online). Phonon spectrum and electronic band structure of the ppPv-\textit{Pnma} phase for NaMgF$_3$ (Panels a and b) and GdFeO$_3$ (Panels c and d) under 60 GPa. Note that all the phonons have positive square frequencies (i.e., they are stable) in both NaMgF$_3$ and GdFeO$_3$. Note also that the electronic band gap is direct at the zone-center in NaMgF$_3$ while it is indirect (from $\frac{2\pi}{b}(0 \frac{1}{4} 0)$ to $\frac{2\pi}{c}(0 0 \frac{1}{2})$) in GdFeO$_3$. 
FIG. 2: (Color online). Phase diagram of the $R\text{FeO}_3$ rare-earth ferrites representing critical pressures as a function of the rare-earth ionic radius. This phase diagram only concerns the $\text{Pv-Pnma}$, $\text{pPv-Cmcm}$ and $\text{ppPv-Pnma}$ phases, up to 120 GPa.
FIG. 3: (Color online). Simulated X-Ray Diffraction pattern for polymorphs Pv-Pnma (Panel a), pPv-Cmcm (Panel b), and ppPv-Pnma (Panel c) of NaMgF$_3$ at 55 GPa, for an incident X-ray having a wavelength $\lambda = 0.3344$ Å. The arrows in Panel (c) correspond to the position of the peaks that have been measured and tentatively assigned to the N-phase of NaMgF$_3$ in Ref. [19].
FIG. 4: (Color online). Simulated X-Ray Diffraction pattern for polymorphs Pv-Pnma (Panel a), pPv-Cmcm (Panel b), ppPv-Pnma (Panel c) of NaZnF$_3$ at 30 GPa, for an incident X-ray having a wavelength $\lambda = 0.3738$ Å.
FIG. 5: (Color online). Modification of the pressure range of stability of the Pv-Pnma, pPv-Cmcm and ppPv-Pnma phases in the ABX$_3$ and $A_2$O$_3$ materials under study, when the P2$_1$/m phase discovered in CaRhO$_3$ \cite{25} is incorporated into the calculations.