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Novel type of ferroelectricity in brownmillerite structures: a first-principle study

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First-principles calculations are conducted on two magnetic brownmillerites, namely Ca2Co2O5 and Sr2Co2O5. Both systems possess a previously overlooked polar Pmc21 phase that is low in energy. This ferroelectric state is even predicted to be the ground state of Sr2Co2O5, which therefore renders such material multiferroic. Strikingly, the ferroelectricity associated with this Pmc21 phase involves an original energetic coupling that is linear in the polar mode, quadratic in another distortion and linear in a third mode. Such ferroelectricity is therefore of a novel type, since it differs from previously reported proper, improper, hybrid improper and triggered kinds of ferroelectricity.

Brownmillerite (BM) oxides form a special class of materials that share the A2B2O5 stoichiometry, where A and B are cations. They can be thought to be derived from the common ABO3 perovskite oxides, by replacing 1/6 of oxygen ions by vacancies. Several recent studies have been devoted to brownmillerite oxides [1–8], and have pointed out their potential interest and the possibility that they might present novel phenomena. For instance, a topotactic phase transformation from brownmillerite to perovskite was demonstrated via oxygen storage/release, and provides an effective means for a reversible oxidation and reduction process [6–8]. A reversible and non-volatile electric-field control of a tri-state phase transformation (involving brownmillerite, perovskite and another structure) by a selective dual-ion switch was also recently achieved, inducing striking electrochromic and magnetoelectric effects [9]. Furthermore, room-temperature electric-field control of ferromagnetism through oxygen ion gating was also demonstrated via the use of brownmillerites [10].

Due to the fact that BM oxides have been much less studied than their perovskite counterpart, it is pertinent to ask if other interesting effects await to be discovered in A2B2O5 compounds, especially noting that Ref. [11] revealed that metallic and ferromagnetic (La1/2Ba1/2)CoO3 perovskite can become insulator, antiferromagnetic and even polar when adopting the (La,Ba)Co2O5 stoichiometry. For instance, one may wonder if previously overlooked polar phase(s) can exist in some A2B2O5 brownmillerites for which B is a magnetic ion, which will render such systems multiferroic – which is of obvious interest when recalling that multiferroics are scarce while having a large technological potential [12–15]. If such hypothetical novel polar phase does exist in BM oxides, one would like to determine the nature of its electrical polarization. In other words, is it solely due to an intrinsic polar instability or rather induced by energetic coupling with other modes? If it is the latter, what are these modes, how many are there and what is the analytical form of this energetic coupling? In other words, are BM oxides proper ferroelectrics or rather improper [16], hybrid improper [17–22], or even triggered-type ferroelectrics [23, 24]?

Motivated to resolve these issues, we performed first-principles calculations on two representative compounds of magnetic brownmillerite oxides, namely, Ca2Co2O5 and Sr2Co2O5. It is presently reported that both of these materials do possess a previously overlooked polar phase of low energy, this phase being predicted to be the ground state of Sr2Co2O5. Moreover and strikingly, the analysis of our ab-initio computations reveals that the resulting ferroelectricity of such overlooked phase is of a new type, since it involves an original coupling involving the polar distortion (linearily) and two non-polar modes that appear with quadratic and linear dependencies, respectively.

As detailed in the Supplemental material (SM), we conducted density functional theory calculations [25] within the revised Perdew, Burke, and Ernzerhof functional for solids plus the Hubbard parameter U (PBEsol + U) with $U = 2.5$ eV for Co ions [11, 26]. We also considered spin arrangements that are most common in per-
ovskites, namely, ferromagnetic (FM), A-type antiferromagnetic (A-AFM), C-type antiferromagnetic (C-AFM), and G-type antiferromagnetic (G-AFM). As shown in SM, the G-AFM ordering is numerically found to present the lowest energy in our investigated systems and phases, which is in-line with previous works [27, 28]. We will thus adopt such ordering in the results shown here.

As indicated in the top left of Fig. 1, we start from the ideal perovskite cubic structure and remove one sixth of its oxygen ions to build the high-symmetry Imma state as well as for lower-in-symmetry Ima2, Pnma, Pbcm, and Pmc21 phases of brownmillerites. The tilting pattern of the T1, T2, T3, and T4 oxygen tetrahedra (see text) is emphasized for each of these low-symmetry phases, with red and blue colors representing clockwise and anticlockwise rotation about the z-axis, respectively.

FIG. 1. Schematization of the construction of the ideal brownmillerite structure from the ideal perovskite structure, and resulting relaxations allowing for the formation of the high-symmetry Imma state as well as for lower-in-symmetry Ima2, Pnma, Pbcm, and Pmc21 phases of brownmillerites. The tilting pattern of the T1, T2, T3, and T4 oxygen tetrahedra is in-line with previous works [27, 28]. We will thus adopt such ordering in the results shown here.

Let us now pay attention to the four different oxygen tetrahedra shown in the bottom of Fig. 1, which we denote as T1, T2, T3, and T4. T1 and T2 belong to the same (001) oxygen tetrahedra layer, while T3 and T4 both occur in the subsequent (001) layer containing oxygen tetrahedra. As is the case for octahedral tilting in perovskites, if we chose a given tetrahedron and select a specific rotation about the z-axis (e.g., clockwise), then the nearest corner-sharing tetrahedra belonging to the same (001) layer will rotate in the opposite way (e.g., anti-clockwise) about the same out-of-plane axis. The different z-rotation patterns about T1, T2, T3, and T4 break the Imma symmetry and result in the following structural phases of brownmillerites: (1) the orthorhombic Ima2 phase, when T1 and T2 rotate anti-clockwise while T3 and T4 adopt a clockwise rotation, which constitutes an overall tetrahedra rotation pattern that we will termed here as − − ++; and which corresponds to a mode with symmetry Γ_4^−; (2) the orthorhombic Pnma phase when T1, T2, T3, and T4 all rotate in a clockwise fashion to form the + + ++ tilting pattern that is associated with a X_4^− mode; (3) another orthorhombic phase, but of Pbcm space group, for the + − − + tetrahedra rotation pattern, associated to a Λ_3 mode; and (4) the orthorhombic Pmc21 phase that occurs when three of the four tetrahedra rotate in the same fashion and in opposite way to the fourth tetrahedron generating, e.g., the + + − + tilting pattern for which all the four tetrahedra rotate in a clockwise fashion at the exception of T3 that rotates counterclockwise. Interestingly, the last pattern involves several phonon modes rather than a single one. As indicated in Table I, these simultaneous modes are Γ_4^−, X_4^−, and Λ_3. It is important to note that both the Ima2 and Pmc21 space groups allow for the occurrence of a spontaneous in-plane electrical polarization as a result of their tilting pattern, unlike Imma, Pnma, and Pbcm, which are all paraelectric. It is also worth to realize that the work of Young et al. [4] has already pointed out the existence of the Imma, Ima2, Pnma and Pbcm phases in brownmillerites, but overlooked the possibility of having a Pmc21 state in these materials – probably because the Imma, Ima2, Pnma and Pbcm structures are the result of the condensation of a single mode (in addition to the trivial Γ_4^− symmetric distortion) unlike Pmc21. Note also that oxygen tetrahedral rotations have indeed been observed in various brownmillerites, such as Ca(Al,Fe)O_2[29], CaCrO_2[30], CaFeO_2[31] and SrFeO_2[7, 32].

Technically, we use 36-atom periodic supercells for investigating the Ima2 and Pnma states and 72-atom perovskite supercells for Pbcm and Pmc21. The cell shape, volume and atomic positions of all these supercells are optimized to relax the studied systems and phases. Table I reports the total energy of the relaxed Ima, Ima2, Pnma, Pbcm and Pmc21 states, as well as the corresponding values of the polarization in the case of Ima2

| Table I. Total energy, E, in meV/f.u. (i.e., per 9 atoms) and polarization, P, in μC/cm^2, of the Sr_2Co_2O_5 and Ca_2Co_2O_5 BM oxides having a G-type AFM spin orders in the different studied phases. The zero of energy corresponds to the predicted ground state in both of these systems. The main non-trivial modes of each structural phase are also provided in the first row. |
|---------------------------|----------------|-----------------|----------------|----------------|
|                           | Imma | Ima2 | Pnma | Pbcm | Pmc21 |
| mode                     | Γ_4^- | X_4^- | Λ_3  | Γ_4^- | Λ_3, X_4^- |
| Sr_2Co_2O_5             | E    | 253.2 | 87.0 | 2.6  | 61.0 | 0.0  |
| P                        | 0.0  | 11.6  | 0.0  | 0.0  | 3.5  |      |
| Ca_2Co_2O_5             | E    | 473.3 | 69.2 | 0.0  | 24.5 | 1.8  |
| P                        | 0.0  | 12.9  | 0.0  | 0.0  | 3.7  |      |
and \(Pmc2_1\), for \(Sr_2Co_2O_5\) and \(Ca_2Co_2O_5\). The paraelectric \(Pnma\) and polar \(Pmc2_1\) phases are the lowest-energy states in these two materials, with \(Pnma\) being the predicted ground state of \(Ca_2Co_2O_5\) while it is \(Pmc2_1\) in \(Sr_2Co_2O_5\). Note that, in both cases, the energy differences between the \(Pnma\) and \(Pmc2_1\) structures are minute, of 2-3 meV per formula unit of 9 atoms. Table I also shows that the computed polarization of the predicted \(Pmc2_1\) ground state of \(Sr_2Co_2O_5\) is 3.5 \(\mu C/cm^2\) in magnitude, therefore making \(Sr_2Co_2O_5\) a multiferroic system since it also adopts a G-type antiferromagnetic ordering. Note that several conflicting phases have been suggested for \(Sr_2Co_2O_5\). For instance, Muñoz et al. [27] proposed that the most stable phase at low temperature has the Imma2 symmetry, based on neutron powder-diffraction (NPD) and X-Ray Diffraction spectrum (XRD) measurements combined with calculations; in contrast, Sullivan et al. [28] either supported the \(Pnma\) space group from electron microscopy or \(Imma\) from their NPD data. Our calculations disagree with all these suggestions, since they predict a \(Pmc2_1\) ground state. Such difficulty in determining the precise symmetry of the ground state experimentally may either arise from the similarity of all these phases as regards their XRD spectrum (see Fig. S1 of the SM), or from the previous overlook that \(Pmc2_1\) can also be a low-energy state in BM. Note also that the captions of Fig. S1 of the SM further discuss the exciting possibility that \(Sr_2Co_2O_5\) can be a room-temperature multiferroic, while Fig. S5 and Table S2 of such SM report different magnetoelectric coupling effects in this compound.

To gain even more insight into this new \(Pmc2_1\) state, let us now consider how the energy of these materials varies when the relaxed \(Imma\) structure is distorted according to the most important modes. Up to fourth order, this energy can be written as (see SM for more information)

\[
E = E_0 + \gamma_{0000} Q_{\Gamma_1^+}^4 + \delta_{0211} Q_{\Lambda_3}^2 Q_{\Gamma_4^+} Q_{X_4^-}
+ \beta_{0200} Q_{\Lambda_3}^2 + \beta_{0020} Q_{\Gamma_4^+}^2 + \beta_{0002} Q_{X_4^-}^2
+ \gamma_{1200} Q_{\Gamma_1^+} Q_{\Lambda_3} + \gamma_{1020} Q_{\Gamma_1^+} Q_{\Gamma_4^+} Q_{X_4^-}
+ \gamma_{1002} Q_{\Gamma_1^+} Q_{\Gamma_4^+} Q_{X_4^-}
+ \delta_{4000} Q_{\Gamma_1^+}^4 + \delta_{0400} Q_{\Lambda_3}^4 + \delta_{0040} Q_{\Gamma_4^+}^2 + \delta_{0004} Q_{X_4^-}^2
+ \delta_{2200} Q_{\Gamma_1^+}^2 Q_{\Lambda_3}^2 + \delta_{2020} Q_{\Gamma_1^+}^2 Q_{\Gamma_4^+}^2 + \delta_{2002} Q_{\Gamma_1^+}^2 Q_{X_4^-}^2
+ \delta_{0220} Q_{\Lambda_3}^2 Q_{\Gamma_4^+}^2 + \delta_{0202} Q_{\Lambda_3}^2 Q_{X_4^-} + \delta_{0022} Q_{\Gamma_4^+}^2 Q_{X_4^-}^2
\]

(1)

where \(Q_{\Gamma_1^+}, Q_{\Lambda_3}, Q_{\Gamma_4^+}\), and \(Q_{X_4^-}\) represent the (dimensionless) amplitude of \(\Gamma_1^+, \Lambda_3, \Gamma_4^+,\) and \(X_4^-\) modes, respectively. \(\alpha_{ijkl}, \beta_{ijkl}, \gamma_{ijkl},\) and \(\delta_{ijkl}\) are expansion coefficients (expressed in eV/72 atoms). \(Q_{\Gamma_1^+}^4 = Q_{\Lambda_3}^2 = Q_{X_4^-} = 1\) corresponds to the \(Pmc2_1\) ground state, while the high-symmetry relaxed \(Imma\) phase is characterized by \(Q_{\Gamma_1^+} = Q_{\Lambda_3} = Q_{\Gamma_4^+} = Q_{X_4^-} = 0\). One can, e.g., see that Eq. (1) involves a linear-quadratic coupling (such as \(Q_{\Gamma_1^+} Q_{\Lambda_3}^2\)) between \(\Gamma_1^+\) and each of the other three modes, but also a biquadratic coupling (e.g., \(Q_{\Gamma_1^+}^2 Q_{\Gamma_4^+}^2\)) between any two modes. Equation (1) also possesses an even more complex coupling between the three nontrivial main modes responsible for the occurrence of the \(Pmc2_1\) structure; such a coupling has of the form \(Q_{\Lambda_3}^2 Q_{\Gamma_4^+} Q_{X_4^-}\). The only odd powers appearing in Eq. (1) are all involving \(\Gamma_1^+\), either via the aforementioned linear-quadratic coupling or via the energy solely associated with \(\Gamma_1^+\) (that is \(Q_{\Gamma_1^+}^4\)). As a result of these odd powers and aforementioned couplings, Eq. (1) predicts that the \(Pmc2_1\) ground state should be four times degenerate, that is
\begin{align}
Pmc2_1 \text{ phases for which } (Q^+_{\Gamma_4}, Q_{\Lambda_4}, Q^-_{\Gamma_4}, Q^-_{X_{4^-}}) \text{ is equal to } (1,1,1,1), (-1,-1,1,1), (1,1,1,1) \text{ and } (1,1,-1,1) \text{ should all have the same total energy. Additional density functional theory calculations we performed do confirm such degeneracy. Note that } & Q^+_{\Gamma_4} \text{ and } Q^-_{X_{4^-}} \text{ have the same sign in these degenerate ground states because of the } \\
\Delta\beta Q_{\Gamma_4} & \text{ and quadratic in the main order parameter) } [16]; (iii) \\
\text{discovered bears some resemblance with low-order energy in some commensurate phases}[33]. \text{ It is thus different from (i) proper ferroelectricity (coefficient in front of } & Q^+_{\Gamma_4} \text{ being negative); (ii) improper ferroelectricity (which would typically involve a coupling linear in polarization and quadratic in the main order parameter) } [16]; (iii) \\
\text{triggered-type ferroelectricity which would involve a negative bi-} & \text{quadratic coupling between the polarization distortion and the main order parameter } [23, 24]; \text{ and (iv) even the recently discovered hybrid improper ferroelectricity (for which polarization couples with two other modes via a trilinear coupling)][17–22]. \end{align}

Let us now pay a particular attention to the electrical polarization of the \emph{Pmc2\textsubscript{1}} state, which is along a pseudo-cubic \textless{} 110 \textgreater{} direction. It originally arises from the \emph{\Gamma_4} mode, which is polar in nature because of its associated \textless{} -- + + + \textgreater{} tetrahedral rotation pattern. As shown in Fig. \textsubscript{2b}, the polarization solely associated with the \emph{\Gamma_4} mode (that is, when imposing \textsubscript{1}Q^+_{\Gamma_4} = Q_{\Lambda_4} = Q^-_{X_{4^-}} = 0 \text{ in the calculations}) gives rise to a double well in the energy curve, which is characteristic of proper ferroelectrics. However, Eq. (1) tells us that this \emph{\Gamma_4} mode can also couple with other modes, and that the resulting energy, to be denoted as \emph{\textit{E}}\textsubscript{\textit{Polar}}, and gathering all the terms dependent on \textsubscript{1}Q^\pm_{\Gamma_4} (which is proportional to the magnitude of the polarization) is such as:

\begin{align}
\text{\textit{E}}\textsubscript{\textit{Polar}} = \delta_{0211} Q^+_{\Gamma_4} Q^2_{\Lambda_4} Q^-_{X_{4^-}} + Q^2_{\Gamma_4^-} (\beta_{0020} + \gamma_{1020} Q^\pm_{\Gamma_4^-} + \delta_{2020} Q^2_{\Lambda_4^-} + \delta_{0220} Q^2_{X_{4^-}} + \delta_{0022} Q^2_{X_{4^-}}) + \delta_{0040} Q^4_{\Gamma_4^-} \quad (2)
\end{align}

\begin{align}
The \text{second term of Eq. (2) indicates that the over-} & \text{all harmonic distortion affecting the polar distortion is renormalized by the interaction between the } \text{\Gamma_4 and the other three modes. Such coefficient goes from } \\
\text{\beta_{0020} = -0.28 in the non-interacting case to } & \text{\beta_{0020} + } \\
\text{\gamma_{1020} + } & \text{\delta_{2020} + } \\
\text{\delta_{0022}} \text{=3.30 in the } \text{Pmc2\textsubscript{1}} \text{ ground state. It thus evolves from slightly negative to a strongly} \\
\text{positive value, indicating that linear-quadratic and bi-} & \text{quadratic couplings have the overall effect of suppressing the} \\
\text{polarization of the } & \text{Pmc2\textsubscript{1} state. In fact, the rea-} \\
\text{reason why such a polar distortion survives is the first term} & \text{of Eq. (2), i.e., the large negative } \delta_{0211} \text{ coefficient. Such} \\
\text{term is linear in the polarization (i.e., in } Q^-_{\Gamma_4^-}) \text{, quadratic} & \text{in } Q_{\Lambda_4^-} \text{ and linear in } Q^-_{X_{4^-}}. \text{The energetic coupling we} \\
\text{discovered bears some resemblance with low-order energy in some commensurate phases}[33]. \text{ It is thus different from (i) proper} & \text{ferroelectricity (coefficient in front of } Q^+_{\Gamma_4^-} \text{ being negative); (ii) improper ferroelectricity (which would typically involve a coupling linear in polarization and quadratic in the main order parameter) } [16]; (iii) \\
\text{triggered-type ferroelectricity which would involve a negative bi-} & \text{quadratic coupling between the polarization distortion and the large negative } \delta_{0020} \text{ parameter (which quantifies the } Q^\pm_{\Gamma_4^-} Q^2_{\Lambda_4^-} \text{ coupling); (ii) the small magnitude of the } \\
\text{negative } & \text{positive sum of } \beta_{0020} + \gamma_{1020} + \delta_{2020} + \delta_{0220} + \delta_{0022}
\end{align}
(which is the overall parameter associated with \( Q_{11}^2 \) in Eq. (2)). Note that items (i)-(iii) are also found when determining the expansion parameters of Eq. (1) from simulations performed with the PBE functional using \( U=2.5 \) eV, as shown in Fig. S4 and Table S1 of the SM. Note also that this value of 3–4 \( \mu \text{C/cm}^2 \) is between one and two orders of magnitude larger than the polarization of some improper ferroelectrics [34–37], while being about the same order as that of other improper ferroelectrics [38, 39]. It is also about one order of magnitude smaller than the polarization of BaTiO\(_3\), a prototypical proper ferroelectric [40]. It is also important to realize that Fig. 2a clearly shows that the condensation of the \( \mathbf{X}_4^- \) mode alone leads to a significant decrease of the total energy, with respect to that resulting from the sole condensation of \( \mathbf{G}_1^\dagger \), \( \Lambda_3 \) or \( \mathbf{G}_4^- \), which demonstrates that \( \mathbf{X}_4^- \) is the (main) primary order parameter of the transition from \textit{Imma} to \textit{Pmc21}. However and as aforementioned, Fig. 2b further indicates that \( \mathbf{G}_4^- \) is also unstable by itself, which can be thought to demonstrate that \( \mathbf{G}_4^- \) is also an active order parameter. Moreover, Equations (1) and (2) and the resulting analysis of Fig. 2a reveal that our discovered novel quadratic-bilinear coupling (of the form \( Q_{11}^2 Q_{13}^3 Q_{X4^-} \)) is also essential to generate the \textit{Pmc21} structure. In other words, the transition from \textit{Imma} to \textit{Pmc21} involves two (intrinsically unstable) order parameters as well as a novel energetic coupling, which further demonstrates its originality.

In summary, we have conducted and analyzed first-principles calculations on two different representatives of BM structure, i.e., \( \text{Ca}_2\text{Co}_2\text{O}_5 \) and \( \text{Sr}_2\text{Co}_2\text{O}_5 \). A previously overlooked polar \textit{Pmc21} state is stable and of low energy in these two magnetic compounds, and is even the ground state of \( \text{Sr}_2\text{Co}_2\text{O}_5 \) — therefore making this compound multiferroic in nature. It is also striking that (i) the high-symmetry \textit{Imma} phase of \( \text{Sr}_2\text{Co}_2\text{O}_5 \) has an intrinsic polar instability that is suppressed when incorporating all the bi-quadratic couplings between the polar \( \Gamma_4^- \) mode and the three nonpolar main modes of \textit{Pmc21}; and (ii) that the occurrence of the polarization in the \textit{Pmc21} state in fact originates from a novel energetic coupling of the form \( Q_{13}^3 Q_{11}^2 Q_{X4^-} \). Such a quadratic-bilinear coupling involving all three non-trivial modes of the \textit{Pmc21} structure differs from those that are typical of proper, improper, hybrid improper and triggered kinds of ferroelectricity, and is therefore indicative of a novel type of ferroelectricity. In fact, we numerically found (see Table S6 of the SM) that such a ferroelectric state is of low energy in several BM structures, such as \( \text{Ca}_2\text{Fe}_2\text{O}_5 \) or \( \text{Sr}_2\text{Fe}_2\text{O}_5 \). Hence, it may be possible to also stabilize it under some special conditions, such as applying electric fields or growing the samples on suitable substrates. We thus hope that the present study will motivate further theoretical and experimental studies on brownmillerites, as a promising family for designing novel functional materials. Note, however, that our calculations do not preclude the possibility of structures that are longer in period than those studied here, or even incommensurate in brownmillerites.

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