Varied roles of Pb in transition-metal PbMO$_3$ perovskites (M=Ti, V, Cr, Mn, Fe, Ni, Ru)

John B. Goodenough and Jianshi Zhou

Materials Science and Engineering Program and Texas Materials Institute, University of Texas at Austin, Austin, TX 78712 USA

Abstract

Different structural chemistries resulting from the Pb$^{2+}$ lone-pair electrons in the PbMO$_3$ perovskites are reviewed. The Pb$^{2+}$ lone-pair electrons enhance the ferroelectric transition temperature in PbTiO$_3$, stabilize vanadyl formation in PbVO$_3$, and induce a disproportionation reaction of Cr$^{IV}$ in PbCrO$_3$. A Pb$^{2+}$ + Ni$^{IV}$ = Pb$^{4+}$ + Ni$^{II}$ reaction in PbNiO$_3$ stabilizes the LiNbO$_3$ structure at ambient pressure, but an A-site Pb$^{4+}$ in an orthorhombic perovskite PbNiO$_3$ is stabilized at modest pressures at room temperature. In PbMnO$_3$, a ferroelectric displacement due to the lone pair electron effect is minimized by the spin-spin exchange interaction and the strong octahedral site preference of the Mn$^{IV/III}$ cation. PbRuO$_3$ is converted under pressure from the defective pyrochlore to the orthorhombic (Pbnm) perovskite structure where Pb – Ru interactions via a common O -2p orbital stabilize at low temperature a metallic $Imma$ phase at ambient pressure. Above $P_c \approx 32$ GPa, a covalent Pb – Ru bond is formed by Pb$^{2+}$ + Ru$^{IV}$ = Pb$^{4+}$ + Ru$^{II}$ electron sharing.
1. Introduction

The PbMO$_3$ perovskites manifest an interplay between the Pb – 6s,6p lone-pair hybrids and the transition-metal MO$_3$ perovskite framework. The classic case of ferroelectricity in PbTiO$_3$ has been well-discussed and understood in the literature. The application of high-pressure synthesis in recent years has made available PbMO$_3$ with M covering almost all 3d transition metals and revived interest in the study of PbRuO$_3$. The relevant features of this MO$_3$ framework with which the Pb$^{2+}$ lone pairs interact are reviewed in the discussion of the properties of each PbMO$_3$ compound.

The geometric perovskite tolerance factor

$$t = (A – O)/[\sqrt{2} (M – O)]$$

\[1\]

where (A – O) and (M – O) are the equilibrium bond lengths, is a useful parameter. Compounds AMO$_3$ with a $t < 1$ can be stabilized in the perovskite structure by a cooperative rotation of the MO$_{6/2}$ octahedra. The versatility of the MO$_3$ framework has provided a wealth of information on the properties of the $d$ electrons in the transition-metal AMO$_3$ perovskites.\(^1\) However, with a $t > 1$, the (M – O) bonds are either stretched beyond their equilibrium length or the structure transforms to a hexagonal polytype.\(^2\) Where the (A – O) bond is more compressible than the (M – O) bond, high pressure lowers the effective tolerance factor to stabilize the cubic perovskite structure, and the cubic perovskite is commonly retained at ambient pressure and temperature. Most of the PbMO$_3$ perovskites are synthesized under high pressure at high temperature.

In a cubic AMO$_3$ perovskite, the oxide-ion orbitals that $\pi$-bond with the M-cation $d$ orbitals also $\sigma$-bond with the larger A cation in the body center of the MO$_3$ framework. Competition for covalent bonding with those O – 2$p$ electrons means that the stronger is the covalent component of the A – O bond, the weaker is the covalent component of the M – O $p_\pi$ bonding and therefore the weaker the interatomic M – O – M interactions via the O – 2$p_\pi$ bonding of the MO$_3$ framework. This competition is particularly significant for PbMO$_3$ perovskites where the $d$ electrons of the MO$_3$ framework are at the crossover from localized to itinerant behavior as a result of the M – O – M interactions; the equilibrium (M – O) bond length is larger for localized than for itinerant $d$ electrons.
The large mass of the Pb atom separates the energies of the 6s and 6p electrons; the 6s electrons are more stable than the 6p electrons because the 6s wave functions have a finite density at the nucleus whereas the 6p wave functions have a node at the nucleus. The larger the mass of the atom, the greater the difference in the screening of the outer s and p electrons from the nuclear charge by the core electrons. As a result, two cation valences are stable: Pb\(^{2+}\) : 6s\(^2\)6p\(^0\) and Pb\(^{4+}\) : 6s\(^0\)6p\(^0\). Hybridization of the 6s and 6p orbitals creates an electron density with its center displaced from the nucleus; and in an oxide, the energy cost to form a 6s,6p hybrid can be more than compensated by the gain in bond energy by the covalent component of the Pb – O bond with the empty hybrid orbital on the opposite side of the nucleus. This hybridization is the origin of the lone-pair phenomenon of a Pb\(^{2+}\) ion in an oxide. However, in a PbMO\(_3\) perovskite, the increased Pb – O covalent bonding competes with \(\pi\)-bonding \(d\)-orbital covalent bonding, which introduces an interplay between the lone pair on a Pb\(^{2+}\) ion and orbital ordering or the strength of the M – O – M interactions in the MO\(_3\) framework. All data of crystal structure and physical properties of PbMO\(_3\) (M= Ti, V, Cr, Mn, Fe, Ni, Ru) reviewed in this article are listed in Table.I

<table>
<thead>
<tr>
<th>PbTiO(_3)</th>
<th>PbVO(_3)</th>
<th>PbCrO(_3)</th>
<th>PbMnO(_3)</th>
<th>PbFeO(_3)</th>
<th>PbNiO(_3)</th>
<th>PbRuO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry at room temperature</td>
<td>P4mm</td>
<td>P4mm</td>
<td>Pm-3m</td>
<td>P4/mmm</td>
<td>Orthorhombic</td>
<td>Pbnm</td>
</tr>
<tr>
<td>Lattice parameters(Å)</td>
<td>a=3.909(^{\pm})</td>
<td>a=3.80005(^{\pm})</td>
<td>a= 4.0054(^{\pm})</td>
<td>a = 3.8561(^{\pm})</td>
<td>a = 3.908(^{\pm})</td>
<td>a=5.35827(^{11})</td>
</tr>
<tr>
<td>c=4.1526</td>
<td>c= 4.6703</td>
<td>b=3.948</td>
<td>b=3.498</td>
<td>b= 5.46325</td>
<td>c= 7.70741</td>
<td>c= 5.56314</td>
</tr>
<tr>
<td>Physical properties</td>
<td>Ferroelectric</td>
<td>Ferroelectric</td>
<td>Antiferro magnetic</td>
<td>Antiferro magnetic</td>
<td>?</td>
<td>Antiferro magnetic</td>
</tr>
<tr>
<td>(T_c=764) K(^{4})</td>
<td>(T_c=?)</td>
<td>(T_N=245) K(^{8})</td>
<td>(T_N= 40) K(^{9})</td>
<td>(T_N≈ 225) K(^{11})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CD: Charge disproportionation.

2.1 PbTiO\(_3\)

A \(t > 1\) in BaTiO\(_3\) stretches the Ti – O bond lengths to make the symmetric O – Ti – O bonds along the <100> axes unstable relative to a cooperative, ferroelectric displacement of the Ti\(^{IV}\) towards one of its two neighbors: first along one principal axis, then along two, and finally along all three axes as the temperature is lowered.\(^4\) With a room-temperature \(t = 1\), SrTiO\(_3\)
remains cubic to below room temperature, undergoing a cooperative rotation of the TiO$_{6/2}$ octahedra about a principal axis below 110 K to increase the Sr – O bond energy.$^{15}$ Since the ground state is nearly degenerate with a ferroelectric phase, an $^{18}$O isotope substitution induces a soft-mode phase transition.$^{16}$ Although the size of the Pb$^{2+}$ ion (1.63 Å) is comparable to that of the Sr$^{2+}$ ion (1.58 Å) (tabulated value for XII coordination), nevertheless the difference is large enough to create a $t > 1$ that induces a ferroelectric displacement of the Pb$^{2+}$ by a hybridization of the Pb-6s,6p orbitals. As a result, PbTiO$_3$ undergoes a cooperative ferroelectric displacement of the Ti$^{IV}$ along a single principal axis at a Curie temperature $T_c = 764$ K,$^{17,18}$ significantly higher than $T_c = 393$ K of BaTiO$_3$. $^{19}$ PbTiO$_3$ has a room-temperature axial ratio $c/a = 1.064$ and exhibits a negative thermal expansion to $T_c$ because the cation displacements that enhance the bonding also increase the volume.$^{17,18}$ In PbTiO$_3$, ordering of the lone pair on the Pb$^{2+}$ ions along a principal axis stretches the O-Ti-O bond lengths in this direction to induce the ferroelectric Ti$^{IV}$ displacement. The c-axis O-2$p_{\pi}$ orbitals are not impacted by the high-temperature transition of the Pb$^{2+}$ lone-pair hybrid orbitals; only those in the basal plane. The interplay between the lone-pair ordering on the Pb$^{2+}$ and the ferroelectric Ti$^{IV}$ displacements of the TiO$_3$ framework yields a high ordering temperature and restricts the Ti$^{IV}$ displacement to a single axis. The ferroelectric displacement in PbTiO$_3$ has been fully justified by the density functional theory (DFT); readers are referred to Ref.20 for more detailed information.

### 2.2 PbVO$_3$

An octahedral-site V$^{IV}$ has a single $d$ electron in a threefold-degenerate manifold of $\pi$-bonding orbitals. In the perovskites CaVO$_3$ and SrVO$_3$, the V-O-V interactions are strong enough to create an itinerant-electron band 1/6-filled; these perovskites are metallic.$^{21}$ On the other hand, the single $d$ electron per Ti$^{III}$ in the RTiO$_3$ perovskites (R = Y or a rare earth) are localized.$^{22}$ The smaller $\Delta E$ to transfer an O-2$p_{\pi}$ electron to an empty $\pi$-bonding $t_2$ orbital of V$^{IV}$ enhances the covalent contribution to the V-O bond, thereby increasing the interatomic V-O-V interactions.

Whereas the orbital degeneracy of a localized-electron manifold is removed by a cooperative Jahn-Teller orbital ordering, as is illustrated in the RTiO$_3$ perovskites, the itinerant-electron orbital degeneracy of a V$^{IV}$ may be removed by formation of the vanadyl ion (V = O)$^{2+}$ in which the $d$ electron is ordered into a plane perpendicular to the V = O bond axis. The vanadyl
formation places the V$^{IV}$ in a square-pyramidal site with five rather than six near-neighbor oxide ions.

This situation is well-illustrated by VO$_2$, which crystallizes in the rutile structure, but undergoes a first-order metal-insulator transition below 340 K. The low-temperature monoclinic phase is characterized by a cooperative shift of the V$^{IV}$ ions perpendicular to the c axis to form short V = O bonds with an ordering of the single $d$ electron per V$^{IV}$ into a narrow c-axis band that is split in two by a charge-density wave of V-V dimers containing V-V bonding across shared site edges.\(^1\)

With this background, we now look at the structure of PbVO$_3$ prepared under high pressure at high temperature.\(^5\) The lattice instabilities associated with the lone-pair ordering on the Pb$^{2+}$ together with lattice instabilities associated with orbital degeneracies stabilize competitive phases in attempts at ambient-pressure synthesis. Nevertheless, under high pressure at high temperature, the PbVO$_3$ phase is preferred and is retained on removal of the pressure at room temperature. Like PbTiO$_3$, the high-pressure PbVO$_3$ phase is tetragonal under ambient conditions with the V atoms displaced from symmetric O-V-O bonding along the c-axis; but where PbTiO$_3$ has a room-temperature axial ratio c/a = 1.062, PbVO$_3$ has a much larger c/a = 1.229 as a result of formation of the vanadyl (V = O)$^{2+}$ ion.\(^5\) The tetragonal PbVO$_3$ structure is shown in Fig. 1. The single $d$ electron per V$^{IV}$ is localized and ordered into the $xy$ orbital in the basal plane; the in-plane interatomic V-O-V interactions between the localized-electron spins give a broad maximum in the paramagnetic susceptibility near 200 K\(^6\) typical of 2D antiferromagnetic interactions.\(^{24}\)
Since the high-pressure synthesis at high temperature favors the PbVO$_3$ phase, it provides a means of obtaining a nearly pure PbVO$_3$ phase. Once this phase is quenched to ambient pressure and room-temperature, a natural next step is to investigate what happens to this tetragonal phase when it is subjected to high pressure at room temperature. High pressure can be expected to change the V$^{IV}$ coordination from square-pyramidal to octahedral by a reduction of both the $c$-axis V displacements from an asymmetric to a symmetric bond and by suppression of lone-pair $6s,6p$ hybridization until a cubic PbVO$_3$ perovskite structure is attained. It took 10 years for this investigation to be performed, and then the motivation was a search for a new high-temperature superconductor. However, this investigation proves to be of fundamental importance for our understanding of the transition in a single-valent oxide from localized to itinerant $d$-electron behavior. In the Mott-Hubbard scenario, the dynamics of electron lattice interactions is neglected; orbital degeneracies are removed by the itinerant-electron dispersion curve of width $W$, and the electron-electron correlation energy $U$ associated with excitations of electrons to atomic states of lower positive valence is able to open a gap in the density of one-electron states where a $U > W$ is realized with a reduced bandwidth $W$. This scenario is the basis of the DFT + U calculations in which $U$ appears as an adjustable parameter. The alternative view for a mixed-valent system is to invoke strong electron-lattice interactions that trap electrons in M-cation sites with (M – O) bond lengths appropriate to the M-cation valence. Alternatively, it has been argued from the Virial Theorem for central-force fields$^{25}$ that the equilibrium (M – O) bond length for
itinerant electrons (Mott-Hubbard scenario) should be smaller than that for localized electrons and, therefore, that there can be a first-order bond contraction at a transition from localized to itinerant electrons in a single-valent system like PbVO$_3$. The DFT + U calculations work well for a single-valent MO$_3$ configuration with itinerant or localized $d$ electrons because a periodic potential is preserved in a single-valent compound. Fig. 2(a) shows the anticipated reduction in the axial ratio c/a of the tetragonal PbVO$_3$ phase under pressure at room temperature over the pressure range $0 < P \leq 2.5$ GPa and Fig. 2(b) shows a first-order phase change between the tetragonal and cubic phase in the interval $1.16 < P < 3.82$ GPa. However, despite a drop in resistivity by 5 orders of magnitude across the transition, this itinerant-electron cubic phase is still semiconductive between 2 and 300K up to 11.3 GPa, indicating a $U > W$. Since cubic SrVO$_3$ is metallic, the data indicate that the Pb$^{2+}$ ion is narrowing the $\pi^*$ bandwidth compared to its width in SrVO$_3$. The availability of the Pb – 6$p^0$ orbitals for covalent bonding with the O-2$p$ orbitals in competition with the V – O2$p$-$\pi$ bond covalence reduces the interatomic V-O-V interactions in cubic PbVO$_3$ relative to its value in cubic SrVO$_3$; this reduction appears to render a $W < U$ in PbVO$_3$, but there is no evidence for either polaronic conduction in cubic PbVO$_3$ or localized-electron orbital order. On removal of the high pressure, the cubic perovskite PbVO$_3$ reverts back to the tetragonal phase in the interval $1.11 < P < 2.02$ GPa, which has prevented the measurement of the magnetic properties of the strongly correlated itinerant-electron phase with $U > W$. Of particular interest would be the extent to which the itinerant-electron dispersion width $W$ suppresses the intraatomic orbital angular momentum and spin relative to that for a localized-electron phase. The RTiO$_3$ system contains a single localized $t_2$ electron per Ti$^{III}$ ion for comparison.$^{22}$
2.3 PbCrO$_3$

Octahedral-site Cr$^{IV}$ has two $d$ electrons per Cr$^{IV}$, which prevents removal of the $d$-state degeneracy by the formation of asymmetric O-Cr-O bonds; therefore, a c-axis ordering of the Pb$^{2+}$ lone pairs can only be stabilized by a single-atom removal of a localized-electron orbital degeneracy on the (CrO$_3$)$_2^-$ framework. The intra-atomic spin-spin interactions responsible for Hund’s highest multiplicity rule on a free Cr$^{IV}$ ion can be expected to narrow the bandwidth $W$ of a cubic (CrO$_3$)$_2^-$ framework and to enlarge the correlation energy $U$ to create a $U > W$; but a $\pi^*$ band $1/3$-filled would be at the crossover from antiferromagnetic to ferromagnetic spin ordering, which can be unstable relative to a charge-disproportionation as is found in metallic Mn. $^{27}$ Nature resolves this problem in ferromagnetic CrO$_2$ by providing a c-axis band as well as a $\pi^*$ band; the $\pi^*$ band is $1/4$-filled, and the remaining electrons are ordered into the c-axis band as localized electrons. The localized-electron spins are aligned parallel to the spins of a ferromagnetic $\pi^*$ band $1/4$-filled. $^{27}$ In a cubic- perovskite (CrO$_3$)$_2^-$ framework, this option is not available. A remaining option for removal of the orbital degeneracy at an octahedral-site Cr$^{IV}$ is a charge disproportionation (CD).

A CD of octahedral-site Cr$^{IV}$ is illustrated by the spinel compound Li[MnCr]O$_4$. $^{28}$ As Li is removed, the Cr$^{III}$ are progressively transformed to Cr$^{IV}$ and the Li vacancies create empty tetrahedral sites in the interstitial space that do not share a face with a neighboring Li$^+$ ion. These

![Fig.2 Lattice parameters as a function of pressure for perovskite PbVO$_3$, data are after Ref. 26](image)
tetrahedral sites can accept a Cr$^{VI}$ cation, which triggers the CD reaction $3\text{Cr}^{IV} = \text{Cr}^{VI} + 2\text{Cr}^{III}$. In a PbCrO$_3$ perovskite, lone-pair hybridizations on the Pb$^{2+}$ can perturb the (CrO$_3$)$_2^-$ framework so as to allow a CD reaction within the framework. The $t^3$ configurations on the Cr$^{III}$ have a localized spin $S = 3/2$.

A cubic PbCrO$_3$ perovskite phase was first stabilized under high pressure at high temperature by Roth and DeVries in 1967, but the structure exhibits several unusual properties. First, its lattice constant $a = 4.00$ Å is significantly larger than that expected based on the equilibrium (Pb – O) bond length for a Pb$^{2+}$ ion. Second, it exhibits a Type-G antiferromagnetic order (all nearest-neighbor spins antiparallel) with a $T_N = 240$ K, nearly three times higher than the $T_N = 90$ K of CaCrO$_3$; CaCrO$_3$ has localized Cr$^{IV}$ $d$ electrons (its tolerance factor is $t < 1$) that are ordered to give Type-C antiferromagnetic order (ferromagnetic $c$-axis interactions). PbCrO$_3$ also has a much higher resistivity and energy gap than are found in CaCrO$_3$ and SrCrO$_3$. In addition, PbCrO$_3$ has a highly irregular peak profile in the powder X-ray diffraction pattern and an unusually high thermal factor at the Cr site characteristic of a static disorder of the Cr atoms. By allowing the Cr atoms to occupy the general Wickoff position 8g $(x,x,x)$ with $x = 0.035$, the overall intensity and peak profile matched well with the structural refinements. Although neutron diffraction does not show evidence of long-range order of the Cr displacements, the refinement of the oxygen positions shows a thermal parameter 10 times larger than is found in other Cr$^{IV}$-containing perovskites: $\text{viz. } 2$ Å$^3$ versus 0.2 and 0.44 Å$^3$. These observations are important experimental clues in support of a CD model, and a DFT + U calculation gave an independent prediction of the CD model.

By allowing the cubic phase of PbCrO$_3$ to expand its volume at room temperature by 10% on removing the high pressure, the calculation showed the volume expansion leads to significant atomic displacements from the ideal cubic positions. Two CD reactions were shown to be close in energy: $3^+ + 3^+ + 6^+$ and $3^+ + 5^+$. The optimized model structure with the $3^+ + 3^+ + 6^+$ configuration is shown in Fig. 3. Pb atoms are displaced substantially towards Cr$^{III}$, which are displaced slightly from the ideal cubic positions. The Cr$^{III}$ and Cr$^{VI}$ are coordinated, respectively, by six and by four oxygen nearest neighbors. In the distorted tetrahedron, there are two short Cr = O bonds and two relatively long Cr-O bonds. The two bond lengths, 1.65Å and 1.78Å are comparable to the 1.59 Å and 1.78Å for the calculated Cr = O and Cr-O bonds in a tetrahedral CrO$_2$(OH)$_2$ cluster in the gas phase. The oxygen bridging to a neighboring Cr$^{III}$ moves towards
the Cr\textsuperscript{VI} to give a long 2.40 Å Cr\textsuperscript{III}-O bond length while the other five Cr-O bonds of Cr\textsuperscript{III} are 2.00 ± 0.05 Å, close to a typical Cr\textsuperscript{III}-O bond length of 2.0 Å in the RCrO\textsubscript{3} perovskites.\textsuperscript{34} The oxygen bridging from the Cr\textsuperscript{III} to the Pb\textsuperscript{2+} form Pb-O bond lengths of 2.43 – 2.56 Å, substantially shorter than the 2.85 Å estimated for the ideal cubic phase. These shorter Pb-O bonds indicate the Pb-6s,6p hybridization plays an important role in stabilizing the CD of the (CrO\textsubscript{3})\textsuperscript{2-} framework.

Fig. 3 The optimized CD model structure with bond length in Å together with the ideal cubic structure shown as faded structure at the background; the data are from Ref.7

Fig. 4 shows the calculated relative energies E per formula unit for the ideal cubic perovskite (blue) and the CD (red) phases of PbCrO\textsubscript{3} as a function of the cell volume \( V \). The application of hydrostatic pressure at room temperature should suppress the CD model in favor of the ideal cubic model. Indeed, with a sample synthesized with laser heating under the pressure of a diamond anvil cell, an earlier report\textsuperscript{35} signaled a large (9.8%) volume and resistivity collapse in a reversible cubic-cubic first-order transition at a \( P_c = 1.4 \pm 0.2 \) GPa at room temperature. The abrupt transition was found at a \( P_c \) near 3 GPa in a sample synthesized with a large-volume press.\textsuperscript{7} In this latter experiment, the large thermal parameters of the diffraction profiles were also found to drop precipitously in the high-pressure phase. The resistivity drops by over two orders of magnitude at \( P_c \); the conductivity of the high-pressure polycrystalline phase was characteristic of a narrow-band conductor with grain-boundary scattering. The magnetic properties of the high-pressure phase have not been determined because this phase is not retained on removal of the pressure.
Fig. 4 The relative energies \( E \) per formula unit (f.u.) for the ideal cubic perovskite (blue) and the CD (red) phases of \( \text{PbCrO}_3 \) as a function of cell volume \( V \); the data are from Ref. 7.

2.4 Solid solutions
Arevalo-Lopez and Alario-Franco \(^{36}\) have investigated the three solid-solution systems \( \text{PbTi}_{1-x}\text{V}_x\text{O}_3 \), \( \text{PbTi}_{1-x}\text{Cr}_x\text{O}_3 \), \( \text{PbV}_{1-x}\text{Cr}_x\text{O}_3 \). The system \( \text{PbTi}_{1-x}\text{V}_x\text{O}_3 \) remains tetragonal for all \( x \) with a continuous increase with \( x \) of the \( c \) axis and volume. The tetragonal to cubic transition decreases from \( T_c = 763 \) K for \( x = 0 \) to 730 K for \( x = 0.2 \), but for \( x \geq 0.3 \), the samples decompose on heating at ambient pressure. The authors suggest there is a percolation threshold for the \( \text{PbVO}_3 \) phase near \( x = 0.3 \). Similarly, a percolation threshold for the \( \text{PbCrO}_3 \) appears near \( x = 0.3 \) in \( \text{PbTi}_{1-x}\text{Cr}_x\text{O}_3 \) and \( \text{PbV}_{1-x}\text{Cr}_x\text{O}_3 \), a tetragonal/cubic two-phase region appearing at \( x = 0.3 \) in the former and an abrupt tetragonal to cubic transition occurring in the interval \( 0.3 < x < 0.4 \) in \( \text{PbV}_{1-x}\text{Cr}_x\text{O}_3 \). The \( \text{Pb}^{2+} \) displacements become disordered at the percolation threshold in the two \( \text{Cr} \) substituted systems.

2.5 \( \text{PbMnO}_3 \)

The octahedral-site \( \text{Mn}^{IV} \) ions of stoichiometric \( \text{PbMnO}_3 \) should have a non-degenerate \( t^3 \) manifold with a localized-electron spin \( S = 3/2 \) if there is no overlap of the \( \text{Mn}^{IV}/\text{Mn}^{III} \) redox energy by the \( \text{Pb}-6s \) states. With no orbital degeneracy to be removed, the \( \text{(MnO}_3)^{2-} \) framework of a cubic \( \text{PbMnO}_3 \) can be expected to resist deformation of the cubic framework by ordering of a lone-pair on the \( \text{Pb}^{2+} \) ions. Except for a reduction of the \( \text{Mn-O-Mn} \) antiferromagnetic
interactions compared to SrMnO$_3$ by a larger competition of the O-2p orbitals for covalent bonding to the Pb$^{2+}$-6p orbitals, the behavior of PbMnO$_3$ might be similar to that of SrMnO$_3$ if the t > 1 does not stabilize a hybridization of the Pb$^{2+}$-6s,6p electrons.

Both SrMnO$_3$ and PbMnO$_3$ have a tolerance factor $t > 1$, and both form a perovskite polytype. Under pressure at high temperature, both compounds crystallize in the 6H polytype in which the AO$_3$ (111) planes of a cubic phase are stacked cubic, cubic, hexagonal along the $c$ axis. Application of higher pressure at high temperature normally converts 6H polytypes to the cubic 3C perovskite structure. Oka et al.\textsuperscript{9} converted the 6H PbMnO$_3$ polytype to the cubic perovskite structure by treating oxygen-stoichiometric 6H PbMnO$_3$ under 15 GPa at 1000°C. Unfortunately the cubic phase obtained was not oxygen-stoichiometric; iodometric titration showed a composition PbMnO$_{2.94(1)}$. SrMnO$_3$ is notoriously sensitive to loss of oxygen,\textsuperscript{37} which stabilizes a mixed-valent phase by the introduction of Mn$^{3+}$; the Mn$^{3+}$ introduces a ferromagnetic component into the MnO$_3$ framework. The small tetragonal ($c/a = 1.017$) distortion of their 3C PbMnO$_{3.8}$ and the reduction of the $T_N$ to 20 K compared to 233 K for oxygen-stoichiometric 3C SrMnO$_3$ cannot be properly interpreted in terms of the relative properties of the Pb$^{2+}$ and Sr$^{2+}$ ions. As a matter of fact, refinement of the synchrotron X-ray diffraction pattern cannot distinguish the polar structure $P4mm$ versus the non-polar structure $P4/mmm$ of the 3C phase. A DFT calculation\textsuperscript{38} indicates that the $P4mm$ phase has a slightly lower energy of the ground state than that in the $P4/mmm$ phase. However, the calculation also predicts the $P4mm$ phase is metallic. It remains to be clarified whether the lone-pair electrons would induce a ferroelectric displacement in oxygen stoichiometric PbMnO$_3$.

2.6 PbFeO$_3$

Tsuchiya et al.\textsuperscript{10} have reported the synthesis of PbFeO$_3$ under high pressure. In comparison with other PbMO$_3$ perovskites, the study of PbFeO$_3$ is incomplete. The report just shows that the X-ray diffraction pattern of the high-pressure product can be indexed by an orthorhombic perovskite cell, indicating a reduction of the tolerance factor to a t < 1 and therefore a transfer of electrons from Pb$^{2+}$ to Fe$^{IV}$. The X-ray photoemission spectra indicate that the valance of iron in PbFeO$_3$ is close to that of the Fe$^{III}$ in LaFeO$_3$. The Fe$^{IV}$/Fe$^{III}$ couple has an energy that favors the reaction Pb$^{2+} + 2$Fe$^{IV} = Pb^{4+} + 2$Fe$^{III}$, but Fe$^{III}$ is stable in the presence of Pb$^{2+}$. This situation is
consistent with the observation of Fe$^{\text{III}}$, but it leaves the valence state of Pb ambiguous: Pb$^{2+}$ + Pb$^{4+}$ versus Pb$^{3+}$-6s$^{-1}$.

2.7 PbNiO$_3$

The Ni$^{\text{IV}}$/Ni$^{\text{III}}$ and Ni$^{\text{III}}$/Ni$^{\text{II}}$ redox energies are at the top of the O-2p bands, and removal of Li from LiNiO$_2$ results in loss of O$_2$ if more than 0.8 Li are removed. It is easier to synthesize PbO$_2$ than NiO$_2$, which favors the reaction Pb$^{2+}$ + Ni$^{\text{IV}}$ $\rightarrow$ Pb$^{4+}$ + Ni$^{\text{II}}$ in PbNiO$_3$. Although Pb$^{4+}$ is stable in octahedral coordination, Inagauma et al. have synthesized an orthorhombic (tolerance factor $t < 1$) perovskite PbNiO$_3$ at 3 GPa and 800°C; the Pb$^{4+}$ is displaced from the center of a (NiO$_3$)$^4$- framework to lower the number of nearest-neighbor oxygen atoms from 12. However, on removal of the pressure at room temperature and heating to only 400 K, the perovskite PbNiO$_3$ transforms irreversibly to the LiNbO$_3$ structure, which also consists of a framework of corner-shared octahedra. In the LiNbO$_3$ structure, the framework is rhombohedral (R-3); the Pb$^{4+}$ are displaced along a [111] axis into an octahedral site. As pointed out and illustrated in Fig. 5, this transformation only requires a rearrangement of the cooperative rotations of the corner-shared octahedra of the framework that is triggered by a different displacement of the Pb$^{4+}$ ions. The LiNbO$_3$ structure of PbNiO$_3$ is more stable at ambient pressure, which is why the transformation is irreversible on thermal cycling. However, under pressure the ambient-pressure PbNiO$_3$ can be converted back to the perovskite structure in which the Pb$^{4+}$ ion has a larger oxygen coordination. The geological literature has recognized that the LiNbO$_3$ structure commonly transforms to perovskite under high pressure.

Fig. 5 Two structural models of PbNiO$_3$. 
2.8 PbRuO₃

A large cubic-field splitting of the $4d$ states stabilizes the low-spin configuration $t_d^4 e^0$ at an octahedral-site Ru$^{IV}$. The Sr$_{1-x}$Ca$_x$RuO$_3$ system can be prepared as perovskites under ambient pressure; the Sr$_{1-x}$Ba$_x$RuO$_3$ perovskites with $x > 0$ have a tolerance factor $t > 1$ and require a high-pressure synthesis to form as cubic perovskites. In ferromagnetic SrRuO$_3$, the $4d$ electrons of the low-spin $t^4 e^0$ manifold are at the crossover between localized and itinerant behavior; the RuO$_3$ framework of the system Sr$_{1-x}$Ca$_x$RuO$_3$ evidences a Griffiths-type ferromagnetism with an eventual vanishing of long-range magnetic order in CaRuO$_3$. The high-pressure Sr$_{1-x}$Ba$_x$RuO$_3$ cubic phase exhibits strong itinerant-electron ferromagnetism; in BaRuO$_3$, there is an abrupt loss of long-range magnetic order at a critical pressure $P_c \approx 8.6$ GPa indicative of a first-order transition of the majority-spin electrons to itinerant behavior like the minority-spin electrons.

Although PbRuO$_3$ has a perovskite tolerance factor $t \leq 1$, PbRuO$_3$ crystallizes at ambient pressure in the oxygen-deficient pyrochlore structure Pb$_2$Ru$_2$O$_7$ with $x \lesssim 1$ in which Pb $- 6s,6p$ hybrids project electron density into the oxygen vacancies. However, PbRuO$_3$ can be stabilized as an orthorhombic ($Pbnm$) perovskite at 9 GPa and 1400°C but this phase transforms at ambient pressure to another orthorhombic ($Imma$) perovskite phase below 90 K. Since cracks are created in the sample during the first-order transition from $Pnma$ to the $Imma$ phase, the $Imma$ phase was initially reported to be an insulator. By synthesizing the PbRuO$_3$ perovskite phase in a Walker-type multianvil module, Cheng et al. were able to obtain a sample with large enough grains to measure the transport properties on a single grain; they showed that the perovskite PbRuO$_3$ becomes a metal in the $Imma$ phase as a result of broadening of the $\pi^*$ band and that the phase change below 90 K under ambient pressure is not caused by changes in the perovskite tolerance factor, but by an interaction between the Pb-$6s,6p$ hybrids and the Ru-$4d$ electrons that broadens the $\pi^*$ band. In the perovskite system Sr$_{1-x}$Pb$_x$RuO$_3$, this interaction broadens the Ru $- 4d$ band to suppress systematically with increasing x the ferromagnetism of SrRuO$_3$, Fig. 6. Plots of the Weiss constant $\theta_{CW}$ and the $\mu_{eff}$ obtained from the paramagnetic susceptibility, Fig. 7(a,b), show that suppression of the long-range magnetic order occurs where $\theta_{CW}$ passes through zero. A power-law analysis of the low-temperature resistivity $\rho (T) = \rho_o + aT^n$ to obtain the x dependence of n is shown in Fig. 7(c); the minimum n at $x = 0.6$ indicates that suppression of the magnetism is associated with the existence of a
quantum critical point (QCP); the second minimum of n(x) at x = 0.9 is a QCP associated with the appearance of the low-temperature Imma phase of perovskite PbRuO$_3$. The low-temperature Imma phase can be suppressed by applying hydrostatic pressure. Kusmartseva et al. have monitored the transition by measuring resistivity $\rho(T)$ under different pressures. They have found that the phase transition temperature $T_t$ lowers gradually as pressure increases; it vanishes at about 5 GPa. The power-law analysis of $\rho(T)$ under different pressures also confirms a QCP at around 5 GPa.

Fig. 6 Phase diagram of Sr$_{1-x}$Pb$_x$RuO$_3$; the data are from Ref. 14
Fig. 7 (a, b) Parameters from fitting the paramagnetic susceptibility to a Curie-Weiss law and (c) temperature dependence of resistivity $\rho$ of Sr$_{1-x}$Pb$_x$RuO$_3$; the inset: n versus x obtained from the power-law analysis of $\rho(T)$; the data are from Ref. 14.

Application of hydrostatic pressure $P$ at room temperature to the PbRuO$_3$ orthorhombic ($Pbnm$) perovskite phase suppresses the transition to the metallic $Imma$ phase at low temperature. More interesting, the room-temperature lattice parameters and volume $V$ of the $Pbnm$ phase show a systematic contraction with $P$ (Fig. 8) until, at a $P_C \approx 32$ GPa, the lattice parameter $a$ jumps and the lattice parameters $b, c$ and volume $V$ drop abruptly at a first-order transition to a lower-symmetry $Pbn2_1$ phase. The volume decrease is about 6%. This behavior contrasts with that of a normal $Pbnm$ perovskite, which transforms under pressure to a higher symmetry $R-3c$ phase.$^{47}$

The PbRuO$_3$ perovskite has an ambient-pressure tolerance factor $t < 1$, and a cooperative rotation of the RuO$_6$ octahedra about a cubic [1-1 0] axis ($b$ axis of orthorhombic $Pbnm$) shifts the Pb atoms from the A-site center to coordinate it with fewer, but closer oxygen-atom nearest-neighbors. The small shift of the Pb atoms results in four Pb-Ru distances across a shared site.
face about 0.05 Å shorter than the average value. A distortion of the octahedral sites accompanies the cooperative rotation of the octahedra. In the \textit{Pbnm} structure with a tolerance factor \( t \) near unity, the principal site distortion is a reduction from 90° of the O₂ – Ru – O₂ bond angle that subtends the rotation axis.\(^\text{14}\) In contrast, the cooperative rotation of highly distorted RuO$_6$ octahedra in the \textit{Pbn2₁} phase of Fig. 9 creates eight different Pb-Ru distances.\(^\text{48}\) Most striking is a single Pb – Ru distance as short as 2.6 Å, about 0.6 Å shorter than the average value, which is reduced only slightly on traversing \( P_c \). Kusmartseva et al.\(^\text{46}\) have also found independently the pressure-induced phase transition at \( P \approx 30 \) GPa by their structural study under high pressure. They have given only the change of lattice parameters on crossing the phase boundary.

A DFT calculation has shown\(^\text{48}\) that the short Pb – Ru bond is the result of an interaction of the Pb$^{2⁺}$ lone-pair electrons with the two holes per Ru in the 4\textit{d}-electron \( \pi^* \) band in a shared-electron reaction Pb$^{2⁺}$ + Ru$^{IV}$ = Pb$^{4⁺}$ + Ru$^{II}$ shifted to the left. Fig. 10 shows the variations with volume in the relative internal energies per formula unit as obtained by the DFT calculation. By fitting the E-V data to the third-order Birch-Murnaghan equation, the enthalpy difference \( \Delta H \) between the two phases (Fig. 10 Inset) clearly demonstrates the phase crossover. A density of states plot of the \textit{Pbnm} phase at ambient pressure shows an overlap of the Pb – 6\textit{s}, Ru – 4\textit{d}, and O-2\textit{p} states in the energy range \( E_F - 3 \) eV < \( E \) < \( E_F + 1 \) eV. The covalent-like Pb – Ru bond formation in the \textit{Pbn2₁} phase leaves the corresponding antibonding orbitals completely empty; \( E_F \) is located at the leading edge of the bonding states, which accounts for the observation that the \textit{Pbn2₁} phase remains a bad metal.
Fig. 8: Lattice parameters as a function of pressure for PbRuO$_3$; the data are from Ref. 48.

Fig. 9: Two structural models of PbRuO$_3$. 

Pbnm  Pbn2$_1$
Fig. 10 Variations in the relative internal energies (E) per formula unit (f.u.) for the *Pbnm* and *Pbn2* phases of PbRuO$_3$ as a function of volume (V) from the LDA calculation. Inset shows the enthalpy difference between the *Pbnm* and *Pbn2* phases ($\Delta H = H_{Pbn2} - H_{Pbnm}$) as a function of pressure (P). The data are from Ref. 48.

3. Conclusions

This review of the observed properties of the PbMO$_3$ perovskites with M=Ti, Cr, Mn, Fe, Ni, and Ru leads to the following conclusions:

(1) A perovskite tolerance factor $t > 1$ for PbMO$_3$ with M=Ti, Cr, Mn, Fe, Ni makes it necessary to use high-pressure synthesis to obtain a cubic 3C perovskite phase. Although PbRuO$_3$ has a $t < 1$, the Pb$^{2+}$ lone pair stabilizes an oxygen-deficient pyrochlore, so here also high-pressure synthesis is needed to obtain a perovskite phase.

(2) Where the cubic phase is stable at ambient temperature and pressure, a $t > 1$ stretches the Pb-O bonds from their equilibrium length to make the phase unstable with respect to a Pb$^{2+}$ displacement from the center of symmetry of its site with an associated hybridization of the Pb-6s,6p orbitals, but creation of a polar state is confined by symmetry to a transition from a cubic to a tetragonal phase. In PbTiO$_3$ and PbVO$_3$ where the M$^{IV}$ cation has a $t^0_2$ or a $t^1_2$ electron configuration, a $t > 1$ also stretches the equilibrium O-M-O bonds to provide cooperative Pb$^{2+}$ and M$^{IV}$ ferroic displacements that transition the lattice from cubic to tetragonal symmetry. The $t^2_2e^0$ configuration on octahedral-site Cr$^{IV}$ prohibits a cooperative ferroic displacement of the Cr$^{IV}$ in a cubic-to-tetragonal transition. In this case, the Cr$^{IV}$ electrons force a non-colinear
displacement of the Pb\(^{2+}\) ions that is cooperative with a charge disproportionation, \(3\text{Cr}^{\text{IV}} = 2\text{Cr}^{\text{III}} + \text{Cr}^{\text{VI}}\), on the CrO\(_3\) sublattice.

(3) As the atomic number of the M atoms increases, the energies of the M\(^{\text{IV}}/\text{M}^{\text{III}}\) and M\(^{\text{III}}/\text{M}^{\text{II}}\) redox energies decrease; where they cross the top of the Pb-6s band, electron transfer from the Pb\(^{2+}\)-6s to the M\(^{\text{IV}}/\text{M}^{\text{III}}\) or even to the M\(^{\text{III}}/\text{M}^{\text{II}}\) redox couple occurs. This electron transfer reduces the perovskite tolerance factor to a \(t < 1\) and an orthorhombic structure in which the Pb-atom displacements are non-ferroic.

(4) With three half-filled \(\pi\)-bonding \(d\) orbitals on M\(^{\text{IV}}\):\(d^3\) ions in octahedral sites, ferroic M\(^{\text{IV}}\) displacements, charge disproportionation, and orbital ordering cannot occur. Moreover, Pb\(^{2+}\) displacements along a tetragonal axis are opposed by M-O-M interactions, which limits a displacement of the Pb\(^{2+}\) ion as has been argued by Hill.\(^{49}\)

(5) Competition between the Pb\(^{2+}\)-6p and the empty M\(^{\text{IV}}\)-3d orbitals for covalent bonding with the O-2p\(_{\pi}\) orbitals of the MO\(_3\) sublattice narrows any \(\pi^*\) band in a single-valent MO\(_3\) perovskite sublattice; this competition may induce a transition from itinerant to localized d-electron behavior. Where the M\(^{\text{IV}}\):\(d^2\) electrons are localized by the band narrowing, applying hydrostatic pressure can induce a first-order transition to itinerant d electrons with a Mott-Hubbard \(U > W\); and applying additional pressure may give a smooth transition to metallic conduction with a \(W > U\).

Acknowledgement
The work was supported by NSF (DMR 1122603) and the Robert A. Welch Foundation (F-1106).

References