Crystallographic Shear Structures as a Route to Anion-Deficient Perovskites**

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Because of the technological importance of perovskite-based oxides, numerous pathways towards new structures have been developed, including ordering at the A and/or B cation sites of the perovskite (ABO₃) structure, vacancy ordering at the anion site, the intergrowth of perovskite and related structures, and the formation of hexagonal perovskite polytypes. However, it has been generally accepted that crystallographic shear (CS) structures cannot be realized in perovskites. CS planes commonly occur in anion-deficient oxides derived from the ReO₃ or rutile (TiO₂) structures, which are based on planes commonly occur in anion-deficient oxides derived from Nb₂O₅ and its Ti-containing derivatives.[2–6] The shear operation in a perovskite framework with time. We also describe the general crystallographic mechanism, leading to a lower coordination number for the A cation sites of the perovskite structure are empty in ReO₃. Usually, the presence of A cations in perovskites favors point defects in the anion sites (in a random or ordered arrangement), leading to a lower coordination number for the B cations, and prevents the elimination of anion point defects by a shear operation.[2] Herein, we report the occurrence of CS structures in perovskite-based “Pb₂Fe₂O₅,” for the first time. We also describe the general crystallographic mechanism of CS-plane formation in a perovskite framework with the A sites filled by cations bearing a lone 6s² electron pair, which involves the elimination of O vacancies by the shear operation and the relaxation of the structure at the CS plane.

We discuss the role of the lone electron pair in directing structure formation, as well as the relationship between the crystallographic orientation of the CS plane and the chemical composition. The discovery of this mechanism opens up new possibilities for the design of novel perovskite-based compounds containing A cations with a lone 6s² electron pair.

“Pb₂Fe₂O₅” (or “PbFeO₂.5”) is expected to be an anion-deficient perovskite of the brownmillerite (Ca₂AlFeO₅) type,[7–9] however, its structure has not yet been determined. Because of the complexity of the structure and the prevalence of domain fragmentation, the only road to solving the structure is by transmission electron microscopy (TEM).

The brighter reflections in the electron diffraction (ED) patterns of “Pb₂Fe₂O₅” (Figure 1a) reveal a perovskite sublattice with a parameter d₀ ≈ 3.9 Å (p denotes the perovskite subcell). Linear arrays of satellite reflections associated with each basic reciprocal lattice node are typical for periodic CS planes. The displacement vector for the CS planes was deduced from the ED patterns as R = 1/2[110], + 1/3[001], by measuring the fractional shifts hR for the satellite reflections (Figure 1b).[10,11] Closer inspection of the [010] ED pattern reveals the incommensurate character of the modulation. The monoclinic unit-cell parameters (denoted by

[**] The work was supported in part by the IAP V-1 program of the Belgian government and by the Russian Foundation for Basic Research (RFBR: 05-03-34812, 06-03-90168). The authors acknowledge Pavel S. Chizhov for the ELF calculations. S.B. is grateful to the Fund for Scientific Research, Flanders.

The fractional-shift method describes the positions of the satellite reflections as H = h + [m + hR]q, where H and h are satellite and basic diffraction vectors, q is the modulation vector, m is the order of the satellite reflection, and R is the displacement vector of the CS planes. The product qR results in the fractional shift of the array of satellites with respect to the position of the basic reflection.

Figure 1. a) [010] ED pattern of “Pb₂Fe₂O₅,” indexed in the perovskite subcell. b) Derivation of fractional shifts hR; empty squares indicate the positions of reciprocal lattice nodes of the perovskite subcell; square brackets denote the modulation vector q; see text for details.
m) for the commensurate approximant are \( \mathbf{a}_m = 3 \mathbf{a}_p + 7 \mathbf{c}_p \), 
\( \mathbf{b}_m = \mathbf{b}_p \), 
\( \mathbf{c}_m = -4 \mathbf{a}_p + \mathbf{c}_p \) \((\mathbf{a}_p = 29.881, \quad \mathbf{b}_p = 3.884, \quad \mathbf{c}_p = 16.062 \text{ Å}, \quad \beta = 98.49^\circ; \text{ space group } C2/m)\). The CS planes are parallel to (100)\(_m\) = (104)\(_p\).

The cation positions in “Pb\(_2\)Fe\(_2\)O\(_5\)” were determined using high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). In the scanning transmission mode, the intensity related to a column of atoms is proportional to \( Z^* \), where \( Z \) is the average atomic number of the projected column. This relationship often allows a straightforward interpretation of HAADF STEM images. The brighter spots on the unfiltered [010] HAADF STEM image of “Pb\(_2\)Fe\(_2\)O\(_5\)” (Figure 2a) are associated with the Pb columns, whereas the weaker spots (difficult to see in Figure 2a) correspond to the projection of the Fe columns. The resulting atomic arrangement of the cations is shown in Figure 3a. The perovskite blocks (outlined by thick dashed lines in Figure 2b) have a length of \( 4 \mathbf{a}_p \) and are mutually shifted along \( \mathbf{c}_p \), by one perovskite unit cell, according to the (104)\(_p\) orientation of the CS plane. Between the perovskite blocks, six-sided channels consisting of six Fe columns surrounding two Pb columns are formed (outlined by thin solid lines in Figure 2b). This arrangement is confirmed by simulations of the [010] HAADF STEM image (Figure 2a).

The new structure is derived from the perovskite structure by a periodic insertion of (104)\(_p\), CS planes with the displacement vector \( \mathbf{R} = \mathbf{R}_0 + \mathbf{R}_1 \), where \( \mathbf{R}_0 = 1/2[110]_p \) and \( \mathbf{R}_1 = 1/3[001]_p \). The \( \mathbf{R}_0 \) shift applied along the (101)\(_p\) plane eliminates the O atoms marked as open squares in Figure 3a. The O atoms at the edges of the perovskite unit cell parallel to \( \mathbf{c}_p \) (gray square in Figure 3a) are not eliminated by the shear operation, but cannot be retained together with the Pb columns, owing to abnormally short Pb–O separations. The \( \mathbf{R}_1 \) displacement introduces columns of edge-sharing FeO\(_5\) square pyramids that are bridged through corner sharing with columns of FeO\(_3\) octahedra (Figure 3b). Pb atoms are positioned inside the resulting channels, where space is available for their lone \( 6s^2 \) electron pairs. However, the \( \mathbf{R}_0 \) shear alone would lead to very short Pb–Pb separations of \( \sqrt{2} \times 2.76 \text{ Å} \) between the Pb atoms within the channels. The displacement \( \mathbf{R}_1 \) increases this distance to 3.56 \( \text{ Å} \) (Figure 3c).

The \( \mathbf{R}_1 \) displacement also distorts the FeO\(_5\) square pyramids, making the coordination environment of the Fe atoms closer to a trigonal bipyramid.

CS planes with high \((h0l)\) indices can be considered as composed of short segments of low-index CS planes, such as the (101)\(_p\), and (001)\(_p\), planes, as the main constituents. The \( 1/2[110]_p(101)\_p\) structure (in which square brackets indicate the displacement vector and parentheses indicate the orientation of the CS plane) contains layers of six-sided channels parallel to (101)\(_p\) (Figure 3d), which are separated by \( n \) perovskite layers, resulting in a \( A_2\text{FeO}_3 + n\text{FeO}_2 \) homologous series. Despite not having been previously considered as a CS structure, Pb\(_{1,33}\)Sr\(_{0,67}\)Fe\(_2\)O\(_5\) (\( A_4\text{Fe}_4\text{O}_{10} \)) corresponds to the second member of this series.\(^{[13]}\)

The \( 1/2[110]_p(001)\_p \) operation could be a conservative shear, since the displacement vector is parallel to the interface plane. However, the \( 1/2[110]_p \) shift along the FeO\(_3\) plane transforms the FeO\(_3\) octahedra into twice as many FeO\(_5\) pyramids along the FeO\(_3\) octahedra. This transformation is illustrated in Figure 3e. The resulting arrangement of the cations is shown in Figure 3a.
square pyramids (Figure 3e). Only half of the square pyramidal sites are occupied by Fe atoms; however, filling the vacant sites by extra Fe atoms would result in a composition of Fe₂O₃ for the layer and an excess of Fe with respect to the overall composition. These double layers of edge-sharing FeO₅ pyramids can be separated by perovskite layers, leading to AFeO₅ + n AFeO₃ homologues. Similar alternating double layers of strongly distorted FeO₅ pyramids and perovskite layers of FeO octahedra occur in Sr₂FeO₁₂⁺ₙ (A₂FeO₃), which can be considered as the n = 1 member of the homologous series.¹³

The 1/2[110]ₚ (104)ₚ CS structure observed for “Pb₂Fe₂O₅” can be broken up as 2(101)ₚ + (101)ₚ + (001)ₚ, resulting in a composition of 3Pb₂FeO₅ + PbFe₂O₄ + 10PbFeO₃ = Pb₁₅Fe₁₆O₃₉, since the perpendicular (101)ₚ and (101)ₚ planes delimit rectangular perovskite blocks of eight FeO₆ octahedra.

Other CS planes, such as (305)ₚ, were also observed for “Pb₂Fe₂O₅” (in the same sample). The corresponding CS structure can be represented as 3(101) + 2(001) with a composition of 3Pb₂FeO₅ + 2PbFe₂O₄ + 10PbFeO₃ = Pb₁₈Fe₂₀O₄₈, because the perovskite layers between the CS planes have an average thickness of two FeO₆ octahedra. The cation composition agrees with the Pb deficiency experimentally determined using energy-dispersive X-ray (EDX) microanalysis (Pb:Fe = 0.90(3):1.00).

The [010] projections of the Pb₁₅Fe₁₆O₃₉ and Pb₁₈Fe₂₀O₄₈ structures are shown in Figure 4; experimental evidence for the structures is presented in Figure 5. Image simulations based on the structures in Figure 4 (Figure 5, insets) are in excellent agreement with the experimental high resolution electron microscopy (HREM) images.

The CS structures in “Pb₂Fe₂O₅” (1/2[110]ₚ (104)ₚ CS plane) and Pb₁₃Sr₁₆Fe₂O₄₆ (1/2[110]ₚ (305)ₚ CS plane) structures; the cubic perovskite unit cell is outlined by thick white lines; simulations of the images (Δf = −275 Å, t = 30 Å (a); Δf = −200 Å, t = 30 Å (b) are outlined by thin white lines. Δf = defocus, t = thickness.

Figure 4. [010] projections of the a) Pb₁₅Fe₁₆O₃₉ and b) Pb₁₈Fe₂₀O₄₈ CS structures; circles Pb, gray polyhedra FeO₆, black polyhedra FeO₅.

Figure 5. [010] HREM images of the a) Pb₁₅Fe₁₆O₃₉ (1/2[110]ₚ (104)ₚ CS plane) and b) Pb₁₃Sr₁₆Fe₂O₄₆ (1/2[110]ₚ (305)ₚ CS plane) structures; the cubic perovskite unit cell is outlined by thick white lines; simulations of the images (Δf = −275 Å, t = 30 Å (a); Δf = −200 Å, t = 30 Å (b) are outlined by thin white lines. Δf = defocus, t = thickness.

It is expected that the building principles derived herein can lead to new perovskite-based compounds, in which the chemical composition is adjusted by varying the orientation of the CS plane and the thickness of the separating perovskite slabs. In the CS structures observed herein, the size of the perovskite slabs between CS planes of a particular orientation is determined by the oxidation state of the Fe cations; thus, a
change in the partial O$_2$ pressure or the synthesis temperature could induce a variety of other possible structures. The power of the new structural principles becomes clear if one considers introducing two types of B cations with different oxidation states and coordination numbers, in addition to an A cation with a lone electron pair, into the perovskite-based structure.

**Experimental Section**

“Pb$_2$Fe$_2$O$_5$” was prepared by annealing PbO and Fe$_2$O$_3$ in a 2:1 ratio in air at 800°C for 210 h. The X-ray diffraction pattern of the product was fit using the Le Bail method, resulting in the parameters:

\[
\begin{align*}
 a &= 3.8879(2), \\
 b &= 3.8838(2), \\
 c &= 3.9386(3), \\
 \beta &= 90.291(6)°, \\
 q &= 0.05760(1)a + 0.12981(2)c, \\
 q &= 1/2, \\
 a^* &= 0.12981(2)c, \\
 q &= 1/2, \\
 X &= [1/2, 1/2, 1/2].
\end{align*}
\]

The EDX analysis was performed on a JEOL JSM 5510 electron microscope with an INCA attachment. For the electron microscopy, Philips CM20, Jeol 4000EX, and Jeol 3000F instruments were used. Image simulations were carried out with the MacTempas software. The ELF distribution was evaluated for a model compound of composition PbSrFe$_2$O$_5$, in which the mixed-occupancy (Pb$_{0.33}$Sr$_{0.67}$) position in the perovskite block of the Pb$_{1.33}$Sr$_{0.67}$Fe$_2$O$_5$ structure is fully occupied by Sr. The ELF was determined from the results of density functional theory (DFT) calculations performed using the TB-LMTO-ASA method and the Barth–Hedin exchange-correlation potential\[15\] with the LMTO 4.7 program package.\[16\]

Received: June 20, 2006

Published online:  

Keywords: crystallographic shear · electron microscopy · iron · lead · perovskite phases

Communications

Lead Iron Oxides

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Shear innovation: By analyzing the crystallographic shear (CS) structures of "Pb$_2$Fe$_2$O$_5" (see picture; spheres Pb, polyhedra FeO$_6$/FeO$_5"), new building principles are derived for perovskite-based compounds containing cations with a lone electron pair in the A sites of the perovskite structure. The chemical composition can be adjusted by varying the orientation of the CS planes and the thickness of the perovskite slabs between the planes.