A Polar Corundum Oxide Displaying Weak Ferromagnetism at Room Temperature

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ABSTRACT: Combining long-range magnetic order with polarity in the same structure is a prerequisite for the design of (magnetoelectric) multiferroic materials. There are now several demonstrated strategies to achieve this goal, but retaining magnetic order above room temperature remains a difficult target. Iron oxides in the +3 oxidation state have high magnetic ordering temperatures due to the size of the coupled moments. Here we prepare and characterize ScFeO₃ (SFO), which under pressure and in strain-stabilized thin films adopts a polar variant of the corundum structure, one of the archetypal binary oxide structures. Polar corundum ScFeO₃ has a weak ferromagnetic ground state below 356 K—this is in contrast to the purely antiferromagnetic ground state adopted by the well-studied ferroelectric BiFeO₃.

INTRODUCTION

In recent years, multiferroic materials (specifically materials with permanent magnetization and electrical polarization) have attracted great interest, as controlling the magnetic state through the application of an electric field is an enabling feature for novel technologies.1–5 However, materials with multiferroic order above room temperature are rare due to the contraindicated nature of magnetism and polar order.6,7 The most studied systems currently have very small polarizations (structurally undetectable) that are driven by the onset of magnetic order, which lifts the centers of symmetry present in the paramagnetic state.1,4,5,7 In most of the observed cases, the transitions occur well below room temperature, for room temperature magnetoelectric phenomena, currently the best candidates are the hexaferrites and related phases.3,8,9 Many ferroelectrics are based on d⁰ structures whereas magnetism clearly requires the presence of open shell cations. BiFeO₃ can be seen as an archetype for an alternative approach where two sublattices are combined where one is ferroelectrically active and the other magnetically, though in this case, at least near room temperature, the system is purely antiferromagnetically ordered.10 Given the higher ordering temperatures of antiferromagnets, multiferroics with weak ferromagnetism would show promise in this property control.11,12 A two sublattice approach has proved successful in EuTiO₃13 (where lattice strain in a thin film drives a quantum paraelectric to a ferroelectric phase transition) with the magnetic ordering from Eu⁺ occurring at low temperature. High pressure has been used to convert the layered ilmenite FeTiO₃ into a polar LiNbO₃ polymorph which shows weak ferromagnetism well below room temperature,12 with AF order up to 270 K found in the partially ordered (In₁₋ₓMₓ)MO₃ (M = Fe₁₋ₓMnₓ; x = 0.143)3,4,13 LiNbO₃ phases.14–16 Thus, new approaches are needed to increase the temperature of coexistence. We present an alternative approach to generating polarization and magnetization above room temperature by preparing a new polar polymorph of ScFeO₃ (SFO) using high pressure synthesis and biaxial strain based on the corundum structure, which exhibits weak ferromagnetism with an ordering temperature of 356 K. The reported SFO structure is in contrast to the perovskite-derived ScCrO₃17 and ScVO₃18 which are also formed at high pressure for earlier first transition series cations.
EXPERIMENTAL METHODS

ScFe$_{0.15}$Cr$_{0.85}$O$_3$ ($x = 0$–1) was prepared from stoichiometric mixtures of Sc$_2$O$_3$ (99.999%, Sigma Aldrich), Fe$_2$O$_3$ (99.999%, Alpha Aesar), and Cr$_2$O$_3$ (99.997%, Alpha Aesar) reacted at 1500 °C ($x = 0$), 1480 °C ($x = 0.03$), and 1450 °C ($x = 0.10–1$) at 6 GPa for 5 min in a Pt-lined Al$_2$O$_3$ crucible within a cylindrical graphite furnace in a Walker-type multianvil press and then quenched to room temperature by turning off the voltage supply to the resistance furnace, which reduces the temperature from 1500 to 25 °C in ~2 s. The pressure is maintained during the temperature quenching.

Thin films were grown using a Neocera pulsed laser deposition (PLD) chamber equipped with Staib RHEED. A stoichiometric ScFeO$_3$ ceramic target, made by conventional solid state methods, was used in the PLD at a laser energy of 252 mJ over a spot size of approximately 2–3 mm$^2$. The films were grown in an oxygen partial pressure of 2 mTorr. The substrate was held at the temperature 850 °C and the distance from the target 47 mm. A 30 kV electron beam was used in the RHEED at a current of 1.55 A. During cooling, the partial oxygen pressure was held at 150 Torr.

Powder X-ray diffraction (XRD) data were recorded on instrument ID31 (for $x = 0$ over a range of temperatures, $\lambda = 0.3999$ Å) at ESRF, Grenoble. Anomalous scattering data were collected on instrument 111 at Diamond Light Source (DLS). The sample was loaded on the external surface of a quartz capillary (diameter 0.5 mm) to minimize absorption. A monochromator sample was loaded on the external surface of a quartz capillary colllered on instrument I11 at Diamond Light Source (DLS). The sample was loaded on the external surface of a quartz capillary (diameter 0.5 mm) to minimize absorption. A monochromator sample was loaded on the external surface of a quartz capillary

High resolution X-ray diffraction patterns were then recorded for 2 h each at six selected energies near the Fe K absorption edge: 7.050, 7.080, 7.112, 7.138, 7.165, and 7.190 keV. The six diffraction patterns were fitted simultaneously using the TOPAS software package. The peak shape parameters were constrained to be the same for the six patterns during refinement. Sample absorption was fitted using the Pitschke model for surface roughness in the TOPAS software package.

Neutron powder diffraction (NPD) data were collected on the POLARIS instrument at the ISIS facility, Rutherford Appleton Laboratories. Diffraction data analysis was performed with the GSAS suite of Rietveld analysis programs, using the EXPGUi interface. Magnetic structures were modeled using a P1 magnetic only phase; atomic positions and lattice tensors were fixed/ constrained to maintain the nuclear cell and symmetry. The magnetic models were constructed via the representational analysis of the system using SARAh. Structural figures were generated using VESTA.

Convergent beam electron diffraction (CBED) and energy dispersive spectroscopy (EDS) analyses were performed with a JEOL 2000FX electron microscope. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded on a Tecnai G2 microscope operated at 200 kV. High resolution CBED patterns were fitted simultaneously using the TOPAS software package. The peak shape parameters were constrained to be the same for the six patterns during refinement. Sample absorption was fitted using the Pitschke model for surface roughness in the TOPAS software package.

Mössbauer data were obtained using a conventional constant acceleration Mössbauer spectrometer incorporating a ~25 mCi source of Co$^{57}$ in a Rh matrix. Alternating current and direct current magnetization measurements were carried out with a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer. We have measured the dielectric and ferroelectric properties of the samples which were sandwiched between Ag paste deposited electrodes, in parallel plate geometry. We used an Agilent E4980A LCR Meter to measure the dielectric properties and a Radiant Precision LC Ferroelectric Tester to measure the P-E loops.

Piezoresistance microscopy was measured on a 6 × 6 mm$^2$ scan area using a DCP-11 diamond coated tip (NT-MDT, Moscow, Russia) while measuring amplitude and phase (R and $\theta$). It was undertaken on a Park XE-100 (Park Systems, Suwon, South Korea) with a SR830 lock in amplifier (Stanford Research, CA, USA) with a bias voltage of 5 V, a time constant of 1 ms, and a sensitivity of 100 $\mu$V).

All DFT calculations have been performed using the CRYSTAL09 program. We employed the PBE0 hybrid exchange functional that uses 25% Hartree--Fock exchange; reciprocal space sampling has been performed for all structures using a Monkhorst-Pack grid of 8 × 8 × 8 k-points for all structures. Standard all electron basis sets from the CRYSTAL online database (www. crystal.unito.it) have been used for all elements (indicated by the following labels online: Fe_86$^{86}$-411d41G_towler_1992a, Sc_86$^{86}$-11dG$^{11}$_harrison_2006, O_8$^{8}$-411d11G_valenzano_2006). Full geometry optimizations have been performed for each structure, followed by a series of constant volume optimizations to evaluate the phase diagrams. Enthalpies have been derived from the energy-volume data, by fitting to the second order Birch--Murnaghan equation of state.

Monte Carlo simulations have been performed using an extended Ising model with coupling parameters fitted to a test set of different disordered structures. Sampling has been performed on cells containing 5184 ion pairs. For each temperature, 10000 sampling points, separated by 4 times the correlation length of the simulation, have been used.

RESULTS AND DISCUSSION

Reaction of Sc$_2$O$_3$ with Fe$_2$O$_3$ at 1500 °C for 12 h in air at ambient pressure yields a material adopting the bixbyite structure of Sc$_2$O$_3$ (Figure 1a and Supporting Information Figure S1) which shows weak ferromagnetism with a $T_C$ of 39 K$^{31–35}$ (Figure S2). The bixbyite-type ScFeO$_3$ is an anion vacancy-ordered derivative of fluorspar with a disordered distribution of Sc$^{3+}$ and Fe$^{3+}$. This type of structure is a clear candidate for transition to a denser close-packed structure under high pressure by elimination of anion vacancies. Indeed, it has been previously demonstrated that several bixbyite systems convert to corundum type phases at high pressure and temperature.$^{34,35}$ Reaction of stoichiometric mixtures of Sc$_2$O$_3$ and Fe$_2$O$_3$ at 6 GPa and 1500 °C afforded a material (HP SFO) with a unit cell corresponding to the corundum structure ($a = 5.198(1)$ Å, $c = 14.003(1)$ Å) adopted by $\alpha$-Fe$_2$O$_3$ (Figure 1b); this hexagonal close-packed structure has $\frac{1}{2}$ of the octahedral voids filled by metal cations, which can be considered as dimers of face-sharing MO$_6$ octahedra along the [001] direction of stacking of the close-packed oxide layers, linked by corner-sharing into a three-dimensional framework. Synthesis of the bulk material away from the 1:1 composition in Sc$_{1-x}$Fe$_{1+x}$O$_3$...
adopts the distorted perovskite GdFeO
3 structure at high
pressure 17 (Figure 2b) The HP SFO corundum-like struc-
ture was retained for
x
≤ 0.10 (Figure S5) are significantly more robust, not de-
changing below 800 °C.

SFO thin films (~25 nm thick) were grown on SrTiO
3 (001) substrates using pulsed laser deposition (PLD, 850 °C
deposition temperature, oxygen partial pressure of 2 mTorr)
with an SrRuO
3 buffer layer (typically 3–5 unit cell mono-
layers) through substrate-imposed strain engineering
37 (Figure S6). The lattice mismatch of 2.7% between the
pseudocubic perovskite cell of corundum ScFeO
3 (a
p = 3.802 Å, α = 86.2°; Figure 3d and e) and (001) SrTiO
3 is less than that for the ambient pressure bixbyite structure (14.7% in the 45°
cube on cube configuration). The observed 3.806 Å out-of-
plane lattice parameter (Figure 3a) is consistent with the high-
pressure synthesized bulk material.

The cell is distorted from the bulk cell due to substrate
strain with α determined (Supporting Information p S9) as
89.2° at the substrate film interface. Off-axis reciprocal space
maps (RSM) (Figure 3b) reveal Fe
2O
3 coherently aligned
with ScFeO
3, consistent with EDX measurement of the film
composition as Sc 0.87 Fe1.13 O3, attributed to incomplete
stoichiometry transfer from the target and consistent with
the restricted compositional variation found in bulk high
pressure synthesis. Vertical twin planes separate the film into
columnar domains, originating at misfit dislocations that
relax the epitaxial strain and are present every 4–10 nm
(Figure 3c).

The 1:1 stoichiometric ratio of Sc and Fe observed in HP
SFO suggests ordering of these cations within the dimers
of face-shared octahedra of the corundum lattice. Density
functional theory (DFT) calculations, employing the PBE0
hybrid-exchange functional under periodic boundary condi-
tions, show that structures with only heteronuclear (Sc,Fe)
dimers are at least 1.0 eV per dimer more stable than
structures with homonuclear (2Fe or 2Sc) pairs. Homo-
nuclear dimers are thus expected only in very low
concentration, which explains the lack of solid solutions
away from the 1:1 ratio. However, inverting the position of
Sc and Fe ions within a heteronuclear dimer has much
smaller energetic cost (Supporting Information Table S2)
and is likely to occur extensively; we will henceforth refer to
this defect as the antosite dimer.

Ordered decoration of the corundum lattice with the
energetically favored heteronuclear dimers affords two
candidate structures. The ilmenite structure (Figure 4a, left)
arises when the two cations form alternate layers perpendicular
to c (space group R3). If instead the dimers are arranged to
avoid octahedral edge-sharing by like cations (Figure 4a, right),
we obtain the LiNbO
3 structure with three-dimensional self-
connectivity of each cation (space group R3c). DFT
calculations (Supporting Information pp S11–12) show an
energetic preference of 0.13 eV/formula unit (f.u.) for the R3c
variant.

Convergent beam electron diffraction (CBED) allows
unique determination of point groups and was thus applied
to determine the presence or absence of an inversion
center. CBED on bulk ScFeO
3 revealed the noncentrosym-
tric 3m point group and the presence of c-glide planes in
the structure (Figure 4 and Supporting Information Figure S7)---the

Figure 2. (a) Room temperature XRD patterns for Sc
1−xFe
x+2 O
3 (x = 0, ± 0.024). Diamonds represent peaks for corundum
impurities and dots bixbyite. (b) Room temperature XRD patterns
for ScFe
1−xCr
x O
3 (x = 0, 0.03, 0.10, 0.15, 0.20, 0.50, and 1). The re-
resulting phases for each composition are marked on the right side,
where S stands for a high pressure ScFeO
3-type phase and G for a
GdFeO
3-type phase.

The absence of an extensive solid solution in SFO, in contrast
to In
2O
3−Fe
2O
3 and Ga
2O
3−Fe
2O
3, is unexpected given the
similar size (0.745 and 0.645 Å, respectively) and identical
charge of Sc
3+ and Fe
3+, and this indicates the likely presence
of short-range ordered structural motifs in SFO (as discussed
later).

ScFe
1−xCr
x O
3 (x = 0, 0.03, 0.10, 0.15, 0.20, 0.50, 1) solid
solutions were also investigated with ScCrO
3, which
adopts the distorted perovskite GdFeO
3 structure at high
pressure.17 (Figure 2b) The HP SFO corundum-like struc-
ture was retained for x ≤ 0.10 (reacted at 1500 °C (x = 0),
1480 °C (x = 0.03), and 1450 °C (x = 0.10)). The HP SFO
and GdFeO
3-type structures coexist for x = 0.15 and 0.2.
At x ≥ 0.50, only the GdFeO
3-type phase was formed. For
x = 0, the material starts to decompose on heating; at about
200 °C, the peaks begin to broaden; and by 500 °C, the
material has decomposed into ScFeO
3 and Fe
2O
3 (Figure S3).
Both x = 0.03 (Supporting Information Figure S4) and x = 0.10 (Figure S5) are significantly more robust, not de-
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composing below 800 °C.
The polar nature of ScFeO$_3$ thus suggests some Sc/Fe order in the (Figure 4e and f), indicating that the order of Sc and Fe columns was observed on the experimental images. ScFeO$_3$ is incomplete. Sc ($\text{STEM}$) images due to a difference in the atomic number of scanning transmission electron microscopy (HAADF-projected Sc and Fe columns to be imaged as dots of for the initially 12 coordinate perovskite A cation. The ScFeO$_3$ peak is indexed to the perovskite pseudocubic cell. The breadth of the film peak is assigned to strain gradients moving away from the substrate and the domain structure within the film. The space group and unit cell correspond to those of the ordered LiNbO$_3$-type structure, one would expect the corundum-like structure. Assuming a completely cation-ordered LiNbO$_3$ and multiferroic BiFeO$_3$. These can be described either as cation ordered corundums (see above) or alternatively as a derivative of perovskite, where a combination of ferroelectric $\Gamma^{-}_x$ ($x$,,$x$, shift) cation displacement from the AO$_3$ close-packed layer and $R_T$ ($a'$ -- $a'$) octahedral tilting leads to the creation of an octahedral site for the initially 12 coordinate perovskite A cation. The polar nature of ScFeO$_3$ thus suggests some Sc/Fe order in the corundum-like structure. Assuming a completely cation-ordered LiNbO$_3$-type structure, one would expect the projected Sc and Fe columns to be imaged as dots of different brightness on the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images due to a difference in the atomic number of Sc ($Z = 21$) and Fe ($Z = 26$). However, no noticeable difference in the brightness of the dots associated with the Sc and Fe columns was observed on the experimental images (Figure 4e and f), indicating that the order of Sc and Fe in ScFeO$_3$ is incomplete.

The very similar X-ray and neutron scattering factors of Sc$^{3+}$ and Fe$^{3+}$ prevent unambiguous assignment of the ordering extent, based purely on either neutron or nonresonant X-ray diffraction (qualities of Rietveld fits were insensitive to occupancy). Therefore, anomalous scattering diffraction data at the Fe K edge were collected on the 111 instrument at the Diamond Light Source at six energies near the Fe K absorption edge (Figure 5a). Anomalous scattering experiments exploit the change in the X-ray scattering power of an element as the X-ray wavelength moves through the absorption edge, and they are used here to increase the contrast between Sc and Fe by working at the Fe K edge. The data were refined to a composition [Sc$_{0.54(2)}$Fe$_{0.46(2)}$]$_2$[Sc$_{0.46(2)}$Fe$_{0.54(2)}$]O$_3$(Figure 5b), confirming that only a small degree of order is observed ($8(2)\%$ defined as the difference in occupancy), consistent with the polar symmetry observed in CBED, but lack of observable cation order on the HAADF-STEM images due to the negligibly small difference of the scattering power at these positions. These cation site occupancies were then fixed in the refinement of the neutron and nonresonant synchrotron powder diffraction data. The refined structure and coordination environments are shown in Figure 5c–e with refined coordinates, bond lengths, and angles given in Tables 1 and 2 and the cif file provided in the Supporting Information (where the magnetic moments can be found in the gsas .lst file). The Sc$^{3+}$ site is larger (2.104 Å) than the Fe$^{3+}$ site (2.067 Å), as might be expected from simple ionic radii arguments. This is consistent with the DFT-optimized bond lengths (0 K) of 3 × 2.074 Å, 3 × 2.167 Å (Sc–O) and 3 × 1.953 Å, 3 × 2.152 Å (Fe–O) for a fully ordered structure (Supporting Information Tables S3 and S4). The Sc$^{3+}$ site is also more distorted (3.49% vs 3.39%)—the refined bond lengths are thus consistent with the identified polar order. The magnetic structure is that described for $α$-Fe$_2$O$_3$ above the transition Morin transition. The observed reduced...
moment is consistent with the mean field estimate for $T/T_N = 0.84$ of 2.8 $\mu_B/\text{Fe}^{3+}$. The term “polar corundum” is therefore suggested to reflect the combination of partial cation ordering resulting in a noncentrosymmetric corundum-type structure. In polar corundum $\text{ScFeO}_6$, the distinction between oxygen coordination of the two cation sites is less pronounced than in $\text{LiNbO}_3$ and $\text{BiFeO}_3$ favoring incomplete cation order rather than a perovskite-based description.

The isolation of polar corundum $\text{SFO}$ under high $P/T$ reaction conditions can be understood by DFT calculations of the enthalpy of competing structure types (perovskite, ilmenite, polar corundum, postperovskite (CaIrO$_3$), and YMnO$_3$) in comparison with a mixture of the binary oxides at up to 40 GPa (Figure 6). Ferro- (FM) and antiferromagnetic (AFM) phases have been considered for all structures. Taking only 0 K effects into account (upper diagram), the polar corundum structure is predicted not to form a stable phase. Instead, the mixture of AFM binary oxides is stable up to 10.5 GPa, when it transforms into an AFM perovskite, which finally converts into the CaIrO$_3$ postperovskite structure at pressures above 41 GPa.

Temperature effects on the phase stability arise from configurational and magnetic terms. The enthalpy of the paramagnetic phase is approximated as the mean of the AFM and FM enthalpies of each polymorph. Configurational effects are not important for polymorphs where Fe and Sc are in substantially different environments (perovskite, postperovskite, and YMnO$_3$).

For ilmenite and polar corundum, the results above show that antisite disorder is important. A first order approximation of the entropy can be obtained by describing the material as a solid solution $A_xB_{1-x}$O$_3$ of the Fe–Sc dimers, where A and B correspond to the two possible orientations of each dimer. This entropy leads to a stabilization of 0.105 eV/f.u. at 1773 K for ilmenite and polar corundum. Taking configurational and magnetic terms into account stabilizes the polar corundum structure at modest pressures with respect to the binary oxides (Figure 6).

Antisite disorder in the polar corundum structure has been quantified by a series of Monte Carlo (MC) simulations. Interaction parameters are based on an extended Ising model and have been chosen to reproduce the relative energy of different magnetic phases and antisite defects from the DFT calculations (reported in Supporting Information Table S2). The temperature dependence of antisite disorder with respect to the $R3c$ structure (Figure 6) shows a sharp drop in cation order from 0.82 to 0.54 between 1300 and 1450 K. At the synthesis temperature, the MC model predicts the material to be paramagnetic (neither short nor long-range magnetic order remains appreciable in the magnetic RDF) and gives a composition of $[\text{Sc}_{0.515}\text{Fe}_{0.485}]_\text{O}_3$ of the Fe–Sc dimers, where A and B correspond to the two possible orientations of each dimer. This indicates that increased cation order can be obtained by annealing the material below 1300 K, but the reduced configurational entropy under these conditions provides insufficient stabilization of the polar corundum structure with respect to the binary oxides.

Having ascertained the structural details of SFO as a polar partially disordered phase compatible with ferroic behavior, we measured its functional response to applied electric and magnetic fields. The polarization of the ideal crystal structure is therefore suggested to reflect the combination of partial cation ordering resulting in a noncentrosymmetric corundum-type structure. In polar corundum $\text{ScFeO}_6$, the distinction between oxygen coordination of the two cation sites is less pronounced than in $\text{LiNbO}_3$ and $\text{BiFeO}_3$ favoring incomplete cation order rather than a perovskite-based description.

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The ionic contribution to the polarization was calculated as 4.0 μC cm⁻² with a formal point charge model at the geometry found in the DFT calculations using the program PSEUDO. Experimental measurements made use of

Table 1. Refined Structural Parameters for Polar Corundum ScFeO₃ (R₃c, a = 5.202475(4) Å, c = 14.01449(10) Å, V = 328.4944(25) Å³, χ² = 1.047, Rwp = 6.1%)³⁴

|     | x   | Y   | z   | 100U//U₀ | M (μB) |
|-----|-----|-----|-----|----------|--------|
| Sc1 | 0   | 0   | 0.04769(5) | 0.378(5) |
| Fe1 | 0   | 0   | 0.510(5) | 2.72(4) |
| O1  | 0.3423(2) | −0.0260 (1) | 0.8176(2) | 0.482(4) |
| Fe2 | 0   | 0   | 0.04769(5) | 0.378(5) |
| Sc2 | 0   | 0   | 0.510(5) | 2.72(4) |

³Further details of the refinement can be found in the cif file. Sc1 and Fe2 are 46% occupied whilst Sc2 and Fe1 are 54% occupied as determined from the anomalous scattering experiment. ²Fixed to fix the origin.
domains separated by a zero amplitude domain wall. The image (Figure 7, Figure S11), showing equal amplitude however, clear 180° no response was observed. In some regions of the ceramic, fraction of a high level of structural disorder and small 1300 and 1450 K.

Polar corundum structured ScFeO₃ itself displays poor dielectric characteristics with large and frequency-dependent relative permittivity and loss (Figure S8(a)), together with “dead short” P(E) behavior. Annealing to reduce the oxygen vacancy content proposed as the origin of the high loss is not possible due to the decomposition of SFO. Substitution of Fe³⁺ by Cr³⁺ in ScFe₁₋ₓCrₓO₃ is possible up to x = 0.1 (Figure 2b) and increases the ambient pressure thermal stability, permitting annealing at 750 °C in oxygen for 6 h (Figure S4). This decreases the dielectric loss significantly (tan δ < 0.1 at 1 kHz), and the (relative) dielectric permittivity attains a frequency-independent high frequency limit of 60 above 1 kHz (Figure 8b), within the range reported for BiFeO₃. This is also common for BiFeO₃. Cole–Cole plots for ScFe₁₋ₓCrₓO₃ (x = 0 and 0.1) are shown and discussed in the Supporting Information on page S15. P(E) loops close at high frequencies, suggesting removal of the influence of extrinsic charge carriers, but they do not saturate, reaching 1.4 μC/cm² at 50 kV/cm and 100 Hz (Figure S9 is consistent with alignment of the intrinsic polarization without sufficient field being applied to switch it. Nonsaturated P(E) loops are common in polycrystalline BiFeO₃ and explained in terms of high conductivity or large coercive fields due to pinned domain walls. Ferroelectricity is not demonstrated by these measurements.)

Neutron powder diffraction (NPD) shows that polar corundum ScFeO₃ is magnetically ordered at 300 K, adopting a G-type antiferromagnetic (AFM) structure with antiparallel spins for all nearest neighbors: the observed moment orientation within the close-packed layers is the same as that found in the high temperature phase of α-Fe₂O₅: this orientation permits a weak ferromagnetic (WFM) canting. Alternating current susceptibility measurements on ScFeO₃ in a 5 Oe magnetic field reveal a cusp at 356 K consistent with the onset of antiferromagnetic order (Figure 9; for Cr doped samples, see Figure 10 and Table 3). Below this temperature, the FC and ZFC DC magnetization data measured at 1000 Oe diverge, and hysteresis is observed in M(H) loops (Mₑ reaching 0.0106 μ₀/formula unit at 5 K—this small moment canting would not be directly detectable in the NPD measurement), consistent with weak ferromagnetism occurring simultaneously with the antiferromagnetic order. Similar ordering temperatures and magnetization values were obtained in three distinct samples. The bulk nature of the antiferromagnetic order and coupled WFM is proved by Mössbauer spectroscopy (Figure 9c), which reveals T_N = 360 ± 5 K, consistent with the magnetization data. Mössbauer spectroscopy is a local probe of the magnetic field sensed by each iron nucleus and is thus the technique of choice to avoid confusion by small quantities of highly magnetic impurities, which is a potential

piezoelectric force microscopy (PFM). The combination of a high level of structural disorder and small polarization even within a fully ordered ScFeO₃ makes PFM observation of polar domains difficult, and in general, no response was observed. In some regions of the ceramic, however, clear 180° domains were seen in the PFM phase image (Figure 7, Figure S11), showing equal amplitude domains separated by a zero amplitude domain wall. The small effective d₃₃ of ~0.1 pm V⁻¹ in the ceramic (estimated from a comparison with periodically poled LiNbO₃) reinforces the difficulty of observing the polar domains. PFM spectroscopy was performed on a thin film sample where the PFM amplitude was measured as a function of the ac voltage applied at a single point. The response is ~5 pm V⁻¹ and is linear, as would be expected from a piezoelectric material, as opposed to a quadratic response characteristic of electrostriction that occurs in all materials.

Table 2. Refined Bond Lengths for Polar Corundum ScFeO₃

| FeO₁ | ScO₁ | 9x |
|------|------|----|
| 2.139(27) Å | 2.175(27) Å | 2.032(17) Å |

Figure 6. Calculated enthalpies as a function of pressure for ScFeO₃ polymorphs: polar corundum (blue), perovskite (black), YMnO₃ (purple), ilmenite (red), and postperovskite (green) relative to the binary oxides (yellow). Upper plot: 0 K results, for FM (solid lines) and AFM (dashed lined) phases. Mid plot: 1773 K results, for the binary oxides (yellow). Upper plot: 0 K results, for FM (solid lines) and AFM (dashed lined) phases.
The isomer shift indicates Fe$^{3+}$, and the observation of a quadrupole splitting is consistent with the observed distorted octahedral environment. The absence of a center of symmetry on the Fe–O–Fe exchange path allows weak ferromagnetism via the Dzialoshinskii–Moriya interaction. The antisite defects create local FM moments associated with the ilmenite-like environment.

The simultaneous appearance of WFM with the main AFM order (Figure 9) confirms that WFM is an intrinsic property of SFO. The ordering temperature is an order of magnitude higher than that found in the bixbyite polymorph of ScFeO$_3$ because of the more favorable Fe–O–Fe angles that allow the extremely strong d$^5$–d$^5$ AFM superexchange to operate. The dilution of Fe$^{3+}$ with nonmagnetic Sc$^{3+}$ reduces the magnetic ordering temperature from 948 K in the nonpolar R3c corundum $\alpha$-Fe$_2$O$_3$ to $\sim$360 K in ScFeO$_3$ but the strength of the exchange interaction and retention of the 3D network of Fe$^{3+}$ connectivity in the polar corundum still places the ordering above room temperature. Unlike the case of $\alpha$-Fe$_2$O$_3$ (where canting disappears below the 260 K Morin spin reorientation transition due to changes in the anisotropy aligning the moments along the c-axis), WFM in SFO persists to 5 K. The Cr$^{3+}$-doped compounds on which the permittivity measurements were performed display WFM order above room temperature with coupled $T_N$ and $T_c$ demonstrated by ac and dc magnetization measurements, with both $M_s$ (judged by the low $T$ temperature invariant FC magnetization) and $T_N$ decreasing as the Cr$^{3+}$ content increases (Figure 10, Table 3).

Figure 7. Piezoresponse force microscopy of ScFeO$_3$. (a) Topography. (b) Vertical PFM phase. (c) Point spectroscopy of the vertical piezoresponse amplitude as a function of ac drive amplitude. (d) Vertical PFM amplitude. PFM images a, b, and d were measured on a ceramic sample; PFM spectroscopy c was measured on a thin film sample. White circles highlight two domains of equal amplitude but opposite phase and are separated by a domain wall of zero amplitude.
Figure 8. Frequency dependent dielectric constant and dielectric loss of (a) ScFeO$_3$ and (b) ScFe$_{0.9}$Cr$_{0.1}$O$_3$.

Figure 9. Magnetic behavior of high pressure ScFeO$_3$. (a) Temperature dependence of the ZFC and FC dc susceptibility measured at 1000 Oe, and the real part of the ac susceptibility measured at 5 Oe. (b) Temperature dependence of the saturation magnetization, extracted from the M–H curves, by extrapolating the high-field magnetization. The inset shows a magnified version of 5 and 300 K M(H) data; M(H) measurements at other temperatures, used to construct the $M_{sat}$ vs $T$ plot, are given in Figure S8. (c) Mössbauer spectra recorded at four different temperatures. The green and red subspectra at 350 K represent fits to the ordered and nonordered components, respectively, while the solid lines are guides to the eye.
The susceptibility of ScFe$_1^{-x}$Cr$_x$O$_3$ and ScFeO$_3$ is measured and is intrinsic to its formation. The combination of high pressure (to eliminate vacancies in the bixbyite structure where face-sharing octahedra are absent) and high temperature (to generate sufficient though not complete antisite disorder) is thus required to stabilize the polar corundum structure. In contrast to the high pressure LiNbO$_3$ polymorph of FeTiO$_3$ and both ordered and corundum type (In$_{1-x}$Fe$_x$O$_3$ (M = Fe, Mn, Ni; x = 0.143)) weak ferromagnetism persists above room temperature and polar distortions are maintained at high levels of disorder. The calculated theoretical electrical polarization value is smaller than that of BiFeO$_3$ (60 μC/cm$^2$) while it is 3 orders of magnitude larger than those of multiferroics where a spin spiral breaks the inversion symmetry. The observed $M_s$ at 5 K (0.01 μT) is of the same magnitude (0.008 μT) as the $M_s$ measured for high pressure FeTiO$_3$ at 100 K.

The difference in polarity of the Sc–O and Fe–O bonds, and between Sc$^{3+}$ and Fe$^{3+}$ off-center displacements, thus creates the observed polarization, assigned to the different bonding preferences of d$^0$ Sc$^{3+}$ and d$^5$ Fe$^{3+}$. The Fe$^{3+}$ 3d electrons are connected three-dimensionally in the polar corundum, resulting in magnetic order above room temperature. Calculations show antisite defects to have FM nature, and as in α-Fe$_2$O$_3$, the absence of an inversion center in the Fe–O–Fe superexchange pathway allows weak ferromagnetism to occur simultaneously with the antiferromagnetic long-range order. Unlike corundum-structured α-Fe$_2$O$_3$, weak ferromagnetism in polar corundum ScFeO$_3$ persists to 5 K, consistent with different local environments of the Fe$^{3+}$ moments in the two materials. Polar corundum is thus a platform for the wide-temperature coexistence of polarity and ferromagnetism, as, in contrast to other mechanisms for combining polarity and permanent magnetization above room temperature, it does not rely on symmetry breaking associated with magnetic order, resulting in a polar distortion detectable by both structural and functional (piezoresponse force microscopy) measurements. Further modification of the polar corundum structure based on SFO is required to permit switching of the polarization.

**CONCLUSIONS**

Corundum is an archetypal oxide structure, and the observation of a polar variant in SFO is unexpected. CBED unambiguously demonstrates the polar nature of high pressure ScFeO$_3$, accounted for by partial Sc/Fe order over the two distinct octahedral cation sites. The extent of the cation site order observed is quantitatively consistent with DFT calculations of antisite dimer defect creation enthalpies. The absence of extensive solid solution in both bulk and thin film is consistent with each dimer containing one Sc and one Fe—the small degree of ordering can then be assigned to disorder in the orientation of these dimers—which agrees with the high energy of homoatomic occupation of the face-sharing octahedral dimers in DFT calculations. The resulting heteroatomic dimers have two possible polar orientations, so the observed antisite disorder entropically stabilizes the polar corundum structure and is intrinsic to its formation. The combination of high pressure (to eliminate vacancies in the bixbyite structure where face-sharing octahedra are absent) and high temperature (to generate sufficient though not complete antisite disorder) is thus required to stabilize the polar corundum structure. In contrast to the high pressure LiNbO$_3$ polymorph of FeTiO$_3$ and both ordered and corundum type (In$_{1-x}$Fe$_x$O$_3$ (M = Fe, Mn, Ni; x = 0.143)) weak ferromagnetism persists above room temperature and polar distortions are maintained at high levels of disorder. The calculated theoretical electrical polarization value is smaller than that of BiFeO$_3$ (60 μC/cm$^2$) while it is 3 orders of magnitude larger than those of multiferroics where a spin spiral breaks the inversion symmetry. The observed $M_s$ at 5 K (0.01 μT) is of the same magnitude (0.008 μT) as the $M_s$ measured for high pressure FeTiO$_3$ at 100 K.

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**ASSOCIATED CONTENT**

* Supporting Information

Eleven figures and 4 tables plus gisx list files and powder cif for the final neutron refinement, together with the full author list for ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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