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$Fe_{3-x}InSn_xO_6$ (x = 0, 0.25, 0.5): A family of corundum derivatives with Sn-induced polarization and above room temperature antiferromagnetic ordering

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$Fe_{3-x}InSn_xO_6$ (x = 0, 0.25, 0.5): A family of corundum derivatives with Sn-induced polarization and above room temperature antiferromagnetic ordering

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Chemistry of Materials

centrosymmetric $R\overline{3}c$, but increasing the substitution of closed-shell d ¹⁰ Sn ⁴⁺ induces x =
0.25 and 0.5 to crystallize as noncentrosymmetric R3c. Microprobe measurements
indicate that for $x = 0.25$, 0.5, the substitution of Sn^{4+} is not compensated for by
vacancies, which implies the presence of Fe ²⁺ , as corroborated by X-ray absorption near
edge spectroscopy and single crystal X-ray structure refinements. Neutron powder
diffraction experiments on $x = 0.5$ indicate that, these compounds are canted A-type
antiferromagnets which, like Fe ₂ O ₃ and InFeO ₃ , consist of ferromagnetic layers that stack
antiferromagnetically with a single magnetic transition. Weak ferromagnetic interactions
persist to very high temperatures. Temperature dependent second harmonic generation
measurements on $x = 0.25$ and 0.5 show SHG response with ferroelectric-like hysteretic
maxima that correspond with the respective magnetic transitions, which suggest coupling
of the magnetic and polarization order. These new compounds provide more information
on fine-tuning the electronic, magnetic and structural properties of corundum derived
mutlferroics in the search for tunable high temperature magnetoelectric materials.

INTRODUCTION:

The study of multiferroic materials, with more than one type of stable, switchable long range order such as ferromagnetism and ferroelectricity, are of significant interest from both applications and fundamental science perspectives.^{1,2} From complex fundamental phenomena to practical applications in microwave tuners and field sensors, multiferroics,

and especially magnetoelectrics where order parameters are cross coupled, are of great impact to modern life.³⁻⁵ Nevertheless, predicting materials with these properties, and fine-tuning them through synthesis, has proven to be a significant challenge.⁶

The majority of multiferroic materials, both in theory and in application, thus far have been of the ABO₃ or A₂BB'O₆ perovskite structure type.⁶ In a perovskite, a large A-cation is twelve-fold coordinated by oxygens and fits into the vacancies of a three-dimensional array of corner sharing BO₆ octahedra. The stability of a perovskite at ambient pressure is roughly predicted by the Goldschmidt tolerance factor, t, (t = $\frac{R_A + R_0}{\sqrt{2}(R_B + R_0)}$, where $R_{A/B}$ are the radii of the A and B cations, respectively, and R_O is the radius of the oxygen anion); t = 1 for a "perfect" cubic perovskite. As was first noted in the seminal perovskite ferroelectric, BaTiO₃,⁷ ferroelectricity in perovskites is often driven by hybridization of oxygen 2p electrons with the empty d orbitals on the B-site cations, leading to polar displacements. This electronic driving force is therefore less favorable for (magnetic) transition metal cations with electrons in the d shell. The rational design of perovskite multiferroics is a Herculean task at best, and new design strategies and mechanisms are gaining increased attention.^{8,9,10,11}

Page 7 of 41

Chemistry of Materials

Recently, high pressure high temperature (HPHT) synthesis has allowed for the exploration of corundum (ABO₃) and double corundum (AA'BB'O₆) structure family (t <0.85) as an alternative archetype to the traditional perovskite.¹²⁻¹⁷ In corundum, face sharing dimers of AO₆ and/or BO₆ octahedra along the c axis form edge sharing layers in the *ab* plane. Specific sub types (such as the eponymous corundum R_3^2 , and LiNbO₃ R_3^2 c types) are distinguished by the pattern of dimers-to-vacancies along the [001] direction. While there are some exceptions, HPHT synthesis techniques are typically required to stabilize these low-t materials.¹⁸⁻²² The key to ferroelectric polarization in corundum lies in the dimers. Coulombic repulsions between A and B cations of different sizes/charges cause local polarization when cations displace by different magnitudes from the shared face. Ferroelectric switching occurs when a cation from one dimer migrates through an O₃ face to fill a former vacancy, forming a new dimer with the A/BO_6 octahedron that had previously been separated by a vacancy, leaving a new vacancy in its place.¹⁰ An empty dshell is not required for this migration, and therefore magnetic cations can be inserted in any A/A' or B/B' site.^{10,23,24} For example, Mn_2FeMoO_6 , a polar double corundum ferrimagnet with T_N above room temperature (337 K) has magnetic cations on both the A-(d⁵ Mn²⁺) and B- (d⁵ Fe³⁺, d¹ Mo⁵⁺) sites.¹⁷ Other known polar corundum type materials

with T_C/T_N above room temperature reported thus far include LiNbO₃-type BiFeO₃ (R3c, $T_N = 643 \text{ K}$),²⁵ ScFeO₃ (*R*3*c*, $T_N = 356 \text{ K}$),²⁶ GaFeO₃ (*R*3*c*, $T_N = 408 \text{ K}$),²⁷ and InFeO₃ $(R3c, T_N = 545 \text{ K})$.²⁸ To our knowledge, other reported corundum and double corundum oxides are either centrosymmetric, or have a T_c/T_N below room temperature.² In this work, we present $Fe_{3-x}InSn_xO_6$ (x = 0, 0.25, 0.5), a family of double corundum related compounds made at HPHT (6 GPa, 1400-1450°C). Fe₃InO₆ has been found to be centrosymmetric $R\overline{3}c$ through second harmonic generation (SHG) investigations, but the inclusion of a small amount of closed-shell Sn^{4+} causes the x = 0.25 and 0.5 compounds to order in a LiNbO₃-type R3c polar structure at less than half the pressure required to synthesize the most similar compound above, InFeO₃ (1450°C, 15 GPa)²⁸, and which show a hysteretic SHG response with maxima near their respective magnetic transitions. While it would be reasonable to assume that the incorporation of Sn⁴⁺ must be charge-balanced by Fe³⁺ or In³⁺ vacancies, electron microprobe studies indicate practically ideal

stoichiometries for all species, and X-ray Absorption Near-Edge Spectroscopy indicates the presence of Fe²⁺. Additionally, in 2010 Gauden et al. investigated the doping of Sn⁴⁺ and co-doping Mg²⁺/Sn⁴⁺into antiferromagnetic hematite ($R\overline{3}c$ Fe₂O₃) itself and found that

Chemistry of Materials

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vacancies (maximal substitution ~10% Sn).²⁹ For these reasons, we find it reasonable to hypothesize that Sn^{4+} in $Fe_{3-x}In_xO_6$ is compensated for by some amount of Fe^{2+} . The work presented here, aims to improve the overall understanding of ferroelectricity and possible tuned multiferroicity in above-room-temperature magnets in the corundum structure archetype.

EXPERIMENTAL:

Synthesis

Powders of SnO₂ (Sigma Aldrich, 99.9%), Fe₂O₃, In₂O₃, and Fe (Alfa Aesar 99.998%, 99.99%, and 99.9%, respectively) were weighed in stoichiometric quantities and ground in an agate mortar. The mixed powders were wrapped in platinum foil pressurized to 6 GPa in a Walker-type multi anvil apparatus over 8-12 hours then heated between 1400-1450 $^{\circ}$ C for 0.5-2 hours, with longer times preferred to promote the growth of larger single crystals (up to 1 mm) and shorter times optimized to preserve aggregated dense pellets (appropriate for certain properties measurements). Samples were quenched by turning off power to the heater and depressurized over the course of several hours.

Synchrotron X-Ray Diffraction

Samples were finely ground and characterized by synchrotron powder X-ray diffraction (SPXD) at Argonne National Laboratory's Advanced Photon Source, beamline 11-BM ($\lambda = 0.412749$ Å) via the mail-in service. Structural refinements were performed with TOPAS Academic software.

X-Ray Diffraction

Initial powder X-ray diffraction (PXD) was performed on ground crystals with a Bruker D8 Advance diffractometer.-Single crystal X-ray data (SCXD) were collected with Mo K_{ab} $\lambda = 0.7107$ Å, at room temperature on a single crystal of 0.040 x 0.020 x 0.010 mm³ on a Bruker Smart APEX system with charge-coupled device (CCD) area detector and mono-capillary collimation. The reflection data were corrected for polarization and Lorentz and absorption effects, the latter by use of a multi-scan method with Bruker program TWINABS. Crystallographic details, including transmission factor ranges, are in the SI. The structure was solved with the program SHELXT and refined with SHELXL.^{30,31,32}

Microprobe

Chemistry of Materials

Polycrystalline pressed pellets and large single crystals were embedded into epoxy resin and ground flat on one side before being coated with a thin layer of carbon. Analyses were performed in both point-select and multi-line scan modes on a JEOL JXA Superprobe at Rutgers University or on a Cameca SX-100 with a Princeton Gamma Tech IMIX energy dispersive spectrometer at the American Museum of Natural History in New York.

Second Harmonic Generation

Second harmonic generation (SHG) measurements were performed on a modified Kurtz-NLO system, using a Ti Sapphire regenerative amplifier laser with 800nm central wavelength, 1kHz rep rate, < 100 fs pulse duration. No index matching fluid was used in any of the experiments. Temperature dependent measurements were recorded in both heating and cooling for polycrystalline pressed pellets of x = 0.25 and 0.5 in three sweeps from 300 - 773, 973, and 1073 K for x = 0.25 and two sweeps both from 300-575 K for x= 0.5. Subsequent electron backscatter diffractometry (EBSD) experiments were

performed with an Apero 2 scanning electron microscope.

X-ray absorption near-edge spectroscopy (XANES)

XANES data were collected simultaneously with standards in both transmission and fluorescence modes on beamline 7-BM (QAS) using a Si(111) channel cut monochromator at Brookhaven National Laboratory's National Synchrotron Light Source (NSLS-II). The Standard analysis methods, of pre-/post-edge background subtraction and normalization to unity absorption step at the edge, were used in the data analysis

Magnetic Measurements in Finite Field

Magnetization measurements were carried out in a magnetometer with a superconducting quantum interference device (SQUID). Field Cooled (FC) and Zero Field Cooled (ZFC) magnetic measurements were measured at a temperature range of 5-400 K with an applied magnetic field of 1 T and from 400-800 K at 0.5 T. Isothermal magnetization curves were obtained at 5, 100, 150, and 300 K under an applied magnetic field ranging from 6 T to -6 T.

Specific Heat Capacity

High temperature (35–545 K) specific heat measurements were performed at the Institute of Nanotechnology and Materials Engineering (Gdansk Tech) by a Netzsch DSC 204 F1 Phoenix system. Measurements were undertaken in Al concave crucibles on 18 mg bulk

sample; the system was calibrated by sapphire prior measurements and purged by air during measurements.

<u>Neutron Powder Analysis of x = 0.5</u>

Time-of-flight neutron powder diffraction (NPD) data were collected for x = 0.5 on the WISH diffractometer at the ISIS Neutron and Muon Source.³³ The sample (0.1216 g) was loaded into a 6 mm diameter cylindrical vanadium can sealed with a copper O-ring. 30 minute scans were collected at 300 K and then at 50 K intervals up to 500 K. The sample was then cooled and data collected at 5 K and then at 15 K intervals on warming to 300 K. Rietveld refinements³⁴ were carried out with TopasAcademic software^{35,36} using the higher resolution banks of data (average two theta of 152.8 and 121.6 degrees spanning a dspacing range of $\sim 0.7 - 5.2$ Å) and no peaks of longer d-spacing were observed in lower angle banks of data in the temperature range studied. ISODISTORT³⁷ was used to explore possible magnetic structures. Traces of impurity phases SnO₂, InFe₂O₄, were identified in NPD data and were modelled by Pawley phases. Peaks due to Al from the sample environment were also present in higher angle NPD ($2\theta = 152.8^{\circ}$) data and these were fitted with two Pawley phases.

RESULTS AND DISCUSSION

Synchrotron powder diffraction on $Fe_{3-x}InSn_xO_6$, x = 0, 0.25, 0.5, indicate that x = 0, 0.25, and 0.5 crystallize as either in centrosymmetric $R\overline{3}c$, or noncentrosymmetric R3c(lattice parameters a = 5.1526 Å, c = 13.9359 Å; a = 5.1832 Å, c = 13.9986 Å; a = 5.2125Å, c = 14.0620 Å for x = 0, 0.25, 0.5, respectively (see Figure 1 and SI). Due to limitations of the twin operation of Friedel's law these space groups,³⁸ are indistinguishable by powder diffraction. Subsequent single crystal experiments indicated that there was an approximately equal electron density on both metal sites, implying that there is an equal distribution of iron on both the A and B sites. Additionally, structure factor analyses showed that while x = 0 should reasonably be assigned $R\overline{3}c$, x = 0.25 and 0.5 showed either a noncentrosymmetric or hypercentric distribution, respectively. In Rietveld refinements, x = 0.25 and 0.5 species refined acceptably to either $R\overline{3}c$ or R3c (wR² difference of ~0.5%). Some of this uncertainty, especially concerning structure factors, could be attributed to twinning as these HPHT synthesized samples were seen to be highly susceptible to obverse-reverse twin intergrowths. To determine whether x = 0.25 and 0.5 were centrosymmetric or noncentrosymmetric, x = 0, 0.25, and 0.5 were analyzed via second harmonic generation (SHG), which will be discussed in detail shortly, but which agreed

with single crystal structure factor analyses. Therefore x = 0 was finally assigned $R\overline{3}c$ and





Figure 1 Refinement of $Fe_{3-x}InSn_xO_6$, x = 0.5 SPXD data in *R*3*c*. The experimental pattern is shown in blue, calculated in red, and the difference in grey. Blue ticks indicate the main phase, with an SnO₂ impurity in grey ticks (main peak indicated with asterisk). Inset is an image of one of the crystals grown at HPHT, showing optically continuous anisotropy on a 1 mm scale (left) and the *R*3*c* structure viewed along the a-b plane (right).

X-ray absorption near-edge spectroscopy (XANES) was employed to probe cation valences and their potential Sn-substitution induced changes in the title compound series. Referring to Figure 2a one should note the well-known systematic chemical-shift of the Fe-K main-edge to higher energy in the Fe²⁺-Fe³⁺-Fe⁴⁺ sequence of standard compound spectra. This edge energy up-shift with increasing valence is ubiquitous in XANES measurements and reflects the increase in binding energy with decreased screening. Although local structure contributions to the detailed spectral edge-shape, the chemical shift effect remains apparent. It should be noted that the rapid spectral rise demarcating the chemical-shift for the x = 0 spectrum is consistent with Fe³⁺ and that the x = 0.5 is very clearly shifted somewhat down in energy.

Figure 2b displays the Fe-K pre-edge region, where transition features involving final dstates (quadrupole allowed) and d-p hybridized (dipole allowed) are observed. Here the Coulomb attraction energy between the core hole and final d-state shifts these transitions down into the pre-edge region. Both the structure and the chemical shift of these features serve as confirming indicator of Fe-valence changes. There is a spectral evolution from: a low energy peak-feature in the Fe²⁺ standard spectra; to a bimodal higher energy peakfeature in the Fe³⁺ standard; and to a higher intensity/energy feature in the Fe⁴⁺ standard the bimodal character and chemical shift of the x = 0 pre-edge spectrum is consistent with its Fe³⁺ character. It should be noted that in comparison the x=0.5 pre-edge spectrum is

Chemistry of Materials

broadened on its low-energy side, consistent with a modest Fe²⁺ admixture as in the main edge results.

Figure 2c and 2d display the Sn and In K-edges of these materials. The K-edges of these p-block materials manifest both the typical chemical shift to higher energies with increasing valence along with valence-coupled modifications in the near edge peak feature intensity (involving dipole transitions into final p-states). In Figure 2c the increased chemical shift and peak intensity between elemental-Sn⁰ and Sn⁴⁺O₂ is clear. The close correspondence between the $Sn^{4+}O_2$ and the x = 0.5 and 0.25 spectra unambiguously establishes the Sn^{4+} character of the substitution (the x = 0.25 has been shifted for visibility; otherwise x = 0.5 and 0.25 perfectly overlap). Similarly, in Figure 2d the close correlation between the $In^{3+}O_3$, x = 0 and 0.5 spectra establishes a constant In^{3+} state in the latter two. Thus the XANES results imply that the of Sn⁴⁺ substitution is compensated for by some Fe²⁺ admixture and this was used, in combination with electron microprobe results (Figure S 4), as justification for fixing all sites as fully occupied in SCXRD and SPXD Rietveld refinements.



WO₆, LiFe²⁺PO₄, (Fe³⁺)₃InO₆, La₂Fe³⁺VO₆, and SrFe⁴⁺O_{3-δ} for comparison; (**b**) Fe K preedge of Fe_{2.5}InSn_{0.5}O₆ with the same standards as in (a); (c) the Sn K-edge of Fe_{2.5}InSn_{0.5}O₆ (solid red) and Fe_{2.75}InSn_{0.25}O₆ (dashed green, displaced down) is compared to Sn⁰ and Sn⁴⁺O₂ (note that the x = 0.25 spectra has been displaced for visibility as it overlaps with x = 0.5); (**d**) the In K-edge of Fe_{2.5}InSn_{0.5}O₆ and Fe₃InO₆ is compared to In³⁺²O₃.

Figure 2 Fe K-edge (a) for Fe_{2.5}InSn_{0.5}O₆ (solid red) and various standards: Fe²⁺O, Pb₂Fe²⁺

As mentioned, second harmonic generation was utilized for final space group assignation of $Fe_{3-x}InSn_xO_6$. SHG is an even-order non-linear optical technique which is sensitive to symmetry- especially the presence of an inversion center which destroys the SHG Page 19 of 41

Chemistry of Materials

phenomenon.³⁹ At room temperature, x = 0.25 and 0.5 both showed some degree of illumination when exposed to a linearly polarized incident beam, which indicate that both samples could be noncentrosymmetric, whereas x = 0 showed no SHG signal and was thus assigned centrosymmetric $R\overline{3}c$ (Figure S 3). Much of the SHG active portion of x = 0.25was seen to be at grain boundaries, which could be an indication of surface irregularities or strain effects, so further investigation was warranted.

It is well established that the intensity of SHG response is proportional to nonlinear polarization in SHG-active materials, and that in ferroelectrics this response is both time and temperature dependent.^{40,41} As seen in

Figure 3, temperature dependent measurements for x = 0.5 ($T_N = 432$ K, *vida infra*) show an SHG response which increases with temperature to a maximum between 400-450 K, a behavior which indicates not only that there are polarizable domains in x = 0.5, but that these domains increase their polarization with the application of temperature. The smooth transition is nearly identical in heating and warming, similar to hysteresis observed previously in some ferroelectric materials. There is a second, smaller and more dispersed peak at approximately 525 K in x = 0.5 is reminiscent of the dielectric permittivity anomaly seen in low frequency dielectric measurements of relaxor ferroelectrics. However, several

other possible explanations may be more appropriate, including: a second polar phase transition, as in the case of LiRbSO₄;⁴² other effects such as an anomaly in the linear dielectric function at optical frequencies (as SHG intensity is approximately proportional to the third power of the linear refractive index), domain reorientations in the sample, and potentially some x = 0.25 contamination (due to its position and relative size). The somewhat broad dispersion in both peaks can reasonably be attributed to sample effects, which was a polycrystalline pressed pellet with grains in random, as-grown orientation. As *R*3*c* (point group 3m) is optically uniaxial, SHG should only be observed when the incident polarization has a component along the *c* axis of x = 0.5.⁴³



Figure 3 Temperature dependent second harmonic generation data for x = 0.5 in heating (red circles) and cooling (black squares) showing a maximum response between 400-450

K, near the magnetic transition ($T_N = 432$ K). The second, smaller and more dispersed peak is thought to be due to x = 0.25 contamination in this sample.

A similarly smooth thermal hysteresis is seen in x = 0.25 (Figure 4). Since the room temperature SHG signal in x = 0.25 seemed strongest at grain boundaries and surface defects, temperature dependent SHG measurements were performed in three sweeps on a different polycrystalline sample to rule out strain or surface effects. Each sweep shows a broad maximum similar in shape to x = 0.5. The maximum response occurs at approximately 550 K for sweeps 1 and 3, which corresponds with the magnetic transition $(T_N = 532$ K, which will be discussed shortly). Major features for sweep two are displaced by ~150 K relative to the other sweeps (Figure 4 (b)), however several possibilities exist to explain this displacement, including hysteretic effects in polycrystalline samples, and the change of laser focus leading to a drift of the sampled region of polycrystalline grains.



Figure 4 Temperature dependent second harmonic generation data for x = 0.25 in heating (red) and cooling (black) in sweeps from 300 K to 773K (a), 973 K (b), and 1073 K (c) showing a maximum response transition (550 K). The displacement of the second sweep (b) is most likely attributed to measurement effects or to hysteretic effects in the polycrystalline samples

The peak in SHG activity at 400 - 450 K for x = 0.5 (Figure 3) and at approximately 550 K in x = 0.25 (Figure 4) could indicate a change in the polarization of these materials at their respective temperatures, perhaps related to the onset of antiferromagnetic order below 432 K and 532 K, respectively (Figure 5). The SHG activity at high temperatures (and the suggestion of Sn order from 500 K NPD data of x = 0.5) suggest that x = 0.5 and by extension x = 0.25 adopt the non-centrosymmetric *R*3*c* structure in the entire temperature range studied. Therefore, magnetic order is not needed to explain the loss of inversion symmetry (this is broken by the existing Sn – Fe/In cation order), but magnetic order could still cause a change in polarization in this material. Similar coupling between magnetic order and polarization, caused by magnetostriction, has been observed in corundum-

Chemistry of Materials

derived Mn₂MnWO₆ (*R*3, T_N = 58 K, spontaneous polarization \cong 63.3 µC·cm⁻²)¹⁸: the origin of this coupling was clear from the structural changes observed on cooling through this transition. This contrasts with Fe_{2.5}InSn_{0.5}O₆ for which the nuclear structure seems to change smoothly with increasing temperature (see supplementary material), although further data points close to the transition temperature would be required to rule out such coupling.

Magnetization vs temperature, M(T), experiments were performed in two sets for all samples - the first from 0 - 400 K with H = 0.1 T, the second from 400 - 800 K with H = 0.05 T. (Two sets of measurements were required as a heating attachment must be fitted to the magnetometer to measure above 400 K). In all cases, there is a sharp transition at a T_N (608 K, 532K, and 432 K for x = 0, 0.25, and 0.5, respectively, Figure 5) which is well above room temperature, and which at first appears to be ferro-or-ferrimagnetic. This implies that there are weak ferromagnetic, or canted antiferromagnetic interactions present even at very high temperatures, similar to what is seen in hematite.⁴⁴ In none of the three species is linear Curie-Weiss behavior seen, up to instrument limitations. Instead, there is curvature which increases as the transition temperature approaches. At the highest measurement temperatures, the zero field cooled (ZFC, blue circles) and field cooled (FC,

red squares) overlap, but then soon begin to diverge as the sample is cooled. This divergence is most pronounced in x = 0, where it begins at about 725 K and in x = 0.25, where it begins at about 650 K. For x = 0.5, the ZFC and FC curves do not begin to diverge until below T_N. Magnetization vs field (M(H), Figure 6 and Figure S 6) experiments were performed at various temperatures below 300 K. The magnetization of all species is seen to be low (0.14 μ_B /f.u. for x = 0.5 as seen in Figure 6, for example) and unsaturated at the limits of measurement, typical for antiferromagnetic exchange. For x = 0.5, the largest coercive field (H_c = approximately 0.77 T) is observed at the lowest measurement temperature. While coercivity does decrease with increasing temperature somewhat from 300 K to 200 K, it remains, indicating the continued presence of ferromagnetic or canted ferromagnetic-like interactions. There is no indication in any case of a metamagnetic transition such as spin flop or spin flip up to H = 6 T. M(H) could not be measured above the transition temperature due to limitations of the magnetometer heating attachment.



Figure 5 Magnetization vs temperature curves for x = 0 (**a**), 0.25 (**b**), and 0.5 (**c**) showing a sharp transition at 608, 532, and 432K, respectively. (The apparent second transition at 50 K in **b**. is an artifact of oxygen freezing). The FC and ZFC curves diverge to some degree after T_N , implying the possibility of frustration, and linear Curie-Weiss behavior is not observed above T_N up to 800 K, the limit of measurement. Measurements had to be performed in two sets - the first from 0 – 400 K (at H = 0.1 T) and the second from 400 – 800 K (at H = 0.05 T) due to limitations with the SQUID heating attachment. The differences in FC/ZFC divergence for (**a**) and for 0-400 K for (**b**) can be attributed to the

fact that the 0 - 400 K trial did not heat the sample above the magnetic transition



Figure 6 Magnetization vs field (M(H)) for x = 0.5 from H = -6 T to H = 6 T for T = 5 K,

100 K, 200 K, and 300 K.

Let us for a moment consider hematite ($R\overline{3}c$ Fe₂O₃) as an archetype of both our compounds and other Fe³⁺ containing corundums such as ScFeO₃,²⁶ GaFeO₃,²⁷ and InFeO₃²⁸, perhaps understanding them best as dilutions of the same. Below T_N (\approx 948 K), hematite is a canted antiferromagnet. Spins order in ferromagnetic layers which stack antiferromagnetically along the *c* axis.⁴⁵ A small macroscopic magnetic moment (0.0144 $\mu_B/f.u.)^{44,46-48}$ is observed until just above the Morin transition, T_M. After T_M, pure hematite becomes perfectly antiferromagnetic.⁴⁴ The Morin transition can be suppressed by substituting non-magnetic metals into the lattice, disrupting Fe-O-Fe super-exchange, as in the cases of Sn⁴⁺ doped and Sn⁴⁺/Mg²⁺ co-doped hematite studied by Gaudon et al.²⁹

In our "dilution" compounds, one might expect that the strength of macroscopic magnetic exchange would decrease smoothly with the decrease in magnetic carriers. This is seen in Fe_{3-x}InSn_xO₆ (Figure 7) however, InFeO₃ ($T_N = 545$ K), GaFeO₃ ($T_N = 408$ K), and ScFeO₃ ($T_N = 356$ K), all have different T_N values despite having a 50/50 M³⁺/Fe³⁺ cation ratio. The reduction in T_N in these three polar double corundum compounds instead seems to roughly correlate with increasing deviation of the corner-sharing M-O-M angle from the ideal 180° (138.5°, 130.0°, 129.4°, respectively), which has been previously pointed out in comparison with similar perovskite phases.⁴⁹ Fe_{3-x}InSn_xO₆ does not seem to

Chemistry of Materials

follow this rule. The equivalent M-O-M interlayer exchange angle (Table S 3) is $131.4(3)^{\circ}$ and $131.7(4)^{\circ}$ (for the site with Sn) or $131.2(3)^{\circ}$ and $131.3(4)^{\circ}$ (for the one without) for x = 0.25 and 0.5, respectively. Both x = 0.25 and 0.5 have smaller transition temperatures than x = 0, but larger corner sharing angles ($131.20(6)^{\circ}$ for x = 0). A crucial difference between x = 0, 0.25, and 0.5 and the other species discussed is the nearly equal distribution of magnetic cations on both the A and B sites. This seems to lead to greater magnetic exchange between layers than in InFeO₃, GaFeO₃, or even ScFeO₃ (which is almost in line with our linear distribution) in which M³⁺ and Fe³⁺ do not site-share, and thus a higher T_N.



Figure 7 Plot of the percent Fe content vs transition temperature for x = 0, 0.25, 0.5 (black

circles) compared to: $Fe_2O_3^{44}$ (T_N = 948 K, red circle), InFeO₃²⁸ (T_N = 545 K, purple

square), GaFeO₃²⁷ ($T_N = 408$ K, blue triangle), and ScFeO₃²⁶ ($T_N = 356$ K, green triangle). The blue line is a guide to the eye.

It is clear that the precipitous drop in T_N from x = 0 to 0.5 cannot be attributed to a "perovskitic" octahedral tilt-angle^{50,51} analysis. These species all have Fe mixed in the A and B sites, and similarly small M-O-M angles. The difference between them is the amount of closed shell d¹⁰ ions (In³⁺ and Sn⁴⁺) admixed in the A and B sites. Closed shell d¹⁰ cations on the B/B' sites of antiferromagnetic perovskites have been demonstrated to reduce overall magnetic exchange interactions,⁵² which should reduce T_N . As the increase in the percent of closed shell cations is the least subtle differing factor (other than space group, which does not seem to effect T_N when going from x = 0 to 0.25 thus far), yet the transition temperatures fall by approximately 100 K as d¹⁰ content increases, it appears that this phenomenon applies to the corundum structure family as well.



Figure 8 Temperature dependent specific heat C_p of $Fe_{2.5}InSn_{0.5}O_6$ in the vicinity of the transition. A distinct transition can be seen at 410 K, and no additional anomaly or discontinuity is observed in the vicinity of the anomalous second peak in the SHG measurements (~525 K,

Figure 3).

Specific heat measurements were performed on a dense polycrystalline pellet of x = 0.5As seen in Figure 8, there is a distinct transition at 410 K, the position of which correlates reasonably well with the maximum response seen in the temperature dependent SHG of x = 0.5 (Figure 3), and T_N (432 K). No second anomaly or discontinuity is seen near the peak of the specific heat which would correspond to the anomalous second peak in the temperature dependent SHG at ~525 K. Thus, the specific heat indicates that the phase transition at 410 K dominates, and strongly implies that the magnetic transition and the maximum SHG response are coupled.



Figure 9 Refinement profiles for Rietveld refinement using 5 K NPD data for $Fe_{2.5}InSn_{0.5}O_6$ with *R*3*c* model showing (a) bank 5 (153°) data and (b) bank 4 (122°) data; $R_{wp} = 2.24\%$, $R_p = 1.92\%$ and $\chi^2 = 7.04$; observed, calculated and difference profiles are shown in blue, red and grey, respectively and magnetic scattering is highlighted in green. For (a), and top (blue), upper (green), middle (blue), middle (green), middle (pink), lower (yellow) and bottom (purple) tick marks indicate reflection positions for $Fe_{2.5}InSn_{0.5}O_6$, magnetic phase,

Chemistry of Materials

SnO₂ impurity (main peak at ~44000 μ s, 2.14 Å), InFe₂O₄ phase (main peak at ~44000 μ s, 2.14 Å), Al from sample environment (main peak at ~42000 μ s, 2.01 Å), Al from sample environment (main peak at ~42000 μ s, 2.03 Å) and Al from sample environment (main peak at ~42000 μ s, 2.04 Å), respectively. For (b), top (blue), upper (green), middle (blue), middle (green) and lower (pink) tick marks indicate reflection positions for Fe_{2.5}InSn_{0.5}O₆, magnetic phase, SnO₂ impurity (main peak at ~40000 μ s, 2.14 Å), Al from sample environment (main peak at ~38000 μ s, 2.04 Å) and InFe₂O₄ phase (main peak at ~54000 μ s, 2.14 Å), respectively.

Time-of-flight neutron powder diffraction (NPD) data were collected for InFe_{2.5}Sn_{0.5}O₆ in order to understand the magnetic order and to determine the distribution of Sn between the A and B metal sites.¹ In, Fe and Sn have contrasting neutron scattering lengths (4.065 fm, 9.54 fm and 6.2257 fm respectively), meaning neutrons, unlike X-rays, are sensitive to potential Sn site-ordering. SCXRD data were used to determine the initial distribution of Fe and In/Sn over the two 6a sites of the R3c model. Refinement of 500 K data suggested only a slight ordering of Fe over the two sites (Fe occupancies of 0.59(1) and 0.66(1) were obtained for cation sites A and B (see SI). In subsequent refinements, Fe site occupancies were fixed, and constraints were used to maintain stoichiometry (a single global temperature factor was used for all sites), but otherwise In and Sn were allowed to refine freely. These refinements suggest that In and Sn are almost completely ordered, with Sn preferring the slightly smaller coordination octahedron. The final refinement profiles and full details are given in SI. It should be noted that an acceptable fit was also obtained for an $R\overline{3}c$ model, but this would not be consistent with SHG measurements. Moreover, it would be surprising given that InFeO₃ was recently reported to be noncentrosymmetric.

Below $T_N = 432$ K, strong additional Bragg reflections are observed and, as seen in SI, increase smoothly on cooling. These reflections can be indexed by a magnetic cell of the same dimensions as the nuclear unit cell (e.g. 003 peak at 4.69 Å; 101 peak at 4.30 Å) suggesting a magnetic propagation vector k = (0 0 0). Possible magnetic structures were explored using the web-based ISODISTORT software.⁵ Consideration of possible magnetic ordering modes using mode inclusion analysis⁷ suggested that a good fit was obtained for models with moments in-plane described by m Γ_3 modes on both Fe sites (Supplementary Materials), analogous to the magnetic structure reported for InFeO₃.⁸

Chemistry of Materials

Two similar magnetic structures are possible which differ in the arrangement of Fe moments in (001) planes and allowed out-of-plane components: a model of *Cc* symmetry with moments along [210] relative to the nuclear unit cell, with an out-of-plane antiferromagnetic component (described by irrep m Γ_1) also allowed by symmetry; and a model of *Cc*' symmetry with moments along [100] relative to the nuclear unit cell, with an out-of-plane ferromagnetic component (described by irrep m Γ_2).

These two models both allow for existence of the observed weak ferromagnetic moment perpendicular to the main AFM direction, and both give equivalent fits to the data (Supplementary Materials) which cannot be distinguished by powder diffraction experiments.⁵³ Single crystal measurements (e.g. polarized neutron diffraction or magnetization measurements on single crystals) would be needed to distinguish unambiguously between these models.

Refinements suggested moments of similar magnitudes on both Fe sites and so constraints were used to impose equal moments. The first model of *Cc* symmetry was used in all further analysis. Refinement using 5 K data indicated moments of $3.88(1) \mu_B$ per Fe, lower than that expected for high spin d⁵ Fe³⁺ ions (5.92 μ_B), likely due in part to the reduction of some iron to Fe²⁺ as Sn⁴⁺ is accommodated into the system. The reduction in

the ordered moment could also result from covalency, frustration in the magnetic interactions of canted moments, complex domain effects in the sample, disorder in the nuclear structure, or a combination of these effects. Moments are predominantly in the (001) planes but allowing the out-of-plane AFM component (0.51(6) μ_B) gives a very slight improvement in fit (R_{wp} decreases from 2.24% to 2.23% for this additional parameter) but this can't be confirmed from these data. Refinement profiles and full details are given in Figure 9 and Table S.4, and the magnetic structure is illustrated in Figure 10.



Figure 10 Illustration of magnetic structure of $Fe_{2.5}InSn_{0.5}O_6$ from Rietveld refinement using 5 K NPD data; cation sites (1) and (2) are shown in purple and blue, respectively, and moments represented by arrows; oxide sites are omitted for clarity, and the blue arrows on the ab plane view (right) have been shortened to show the purple arrows below.

Chemistry of Materials

This magnetic structure suggests that AFM exchange between Fe³⁺ ions across the shared face of the AO_6 -BO₆ dimension dominates the magnetic ordering, leading to FM layers which are stacked antiferromagnetically along [001], similar to collinear β -Mn₂InSbO₆.⁵⁴ Sequential Rietveld refinements suggest a smooth increase in unit cell volume on warming (see supplementary material). There is no evidence of a change in magnetic structure, or magnetostriction, from 5 K – 500 K. The magnetic ordering temperature in $Fe_{2.5}InSn_{0.5}O_6$ (~432 K) is close to that observed for InFeO₃ (545 K,⁵⁵ but much higher than that of β - $Mn_2InSbO_6^{54}$, presumably reflecting strong Fe – O - super exchange interactions. The origin of the small ferromagnetic component observed in magnetic susceptibility measurements may be the same as that suggested for a similarly small FM component in InFeO₃ (weak ferromagnetism due to Dzaloshinskii-Moriya interactions in this noncentrosymmetric structure giving a slight canting of Fe³⁺ moments away from this collinear structure).⁵⁵ However, our NPD data are not sensitive to such subtle canting.

CONCLUSION

In conclusion, we have studied the magnetic and structural properties of three new double corundum compounds, $Fe_{3-x}InSn_xO_6$ (x = 0, 0.25, 0.5) prepared at high pressure and

temperature (6 GPa, 1400-1450 °C). All three phases order antiferromagnetically well

above room temperature, with $T_N = 608$, 532, and 432K, for x = 0, 0.25, 0.5, respectively. Powder neutron diffraction investigations on x = 0.5 indicate that their magnetic structure consists of ferromagnetic layers stacked antiferromagnetically along [001]. Fe_{3-x}InSn_xO₆ is sensitive to small substitutions, with just 6.25% Sn⁴⁺ admixture enough to change the space group from centrosymmetric $R\overline{3}c$ to noncentrosymmetric R3c, as confirmed by temperature dependent SHG measurements which showed an SHG response for x = 0.25and 0.5 over the entire temperature measurement range (300-500 °C). Thus, the x = 0.25, 0.5 phases are multifunctional, or possibly multiferroic. Temperature dependent SHG measurements show a peak at T_N for x = 0.25 and 0.5, as does the specific heat for x = 0.5, which suggests coupling between polarization and magnetization. A hysteretic SHG response is observed, as would be expected in a ferroelectric material. Further studies, such as piezoforce microscopy or polarization-field and switching current measurements, would be of interest to explore possible ferroelectric behavior and the origin of magnetoelectric coupling. These new compounds could lead to similar new multiferroic materials with high temperature functionality in the pursuit of magnetoelectric coupling.

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Chemistry of Materials

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ASSOCIATED CONTENT

The following files are available free of charge: detailed structure and neutron refinements, transport data, room temperature SHG figures, microprobe analysis data, as well as additional figures for x = 0.25 and 0 magnetization not shown in main text (pdf), crystallographic information files for x = 0, 0.25, and 0.5 (cif)

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Table of Contents Graphic

