

- a. DOE Award #: SC-0005032; University of Houston, Cornell University
- b. Controlling Magnetic and Ferroelectric Order Through Geometry: Synthesis, Ab Initio Theory, Characterization of New Multi-Ferric Fluoride Materials; Prof. P. Shiv Halasyamani (University of Houston) and Prof. Craig Fennie (Cornell University)
- c. Nov. 3, 2016; Research Period Sept. 1, 2010 - August 31, 2014

a. Description of Accomplishments

We have focused on the synthesis, characterization, and ab initio theory on multi-functional mixed-metal fluorides. With funding from the DOE, we have successfully synthesized and characterized a variety of mixed metal fluoride materials.

- (i) **BaMF₄ (M = Mg, Mn, Co, Ni, and Zn):** A family of materials that has received renewed interest are the mixed-metal fluorides BaMF₄ (M = Mg, Mn, Fe, Co, Ni, and Zn). These iso-structural and crystallographically polar materials – all of the materials crystallize in the polar space group *Cmc2₁* – are ferroelectric at room temperature for M = Mg, Co, Ni, and Zn²² and exhibit anti-ferromagnetic ordering with T_N ~ 20 – 80K for M = Mn, Fe, Co, and Ni. Thus simultaneous ferroelectric *and* anti-ferromagnetic behavior, at low temperatures, may only be observed in BaCoF₄ and BaNiF₄.

Originally, the BaMF₄ family of materials were grown as crystals from the melt of BaF₂ and MF₂ in a HF atmosphere at elevated temperatures – above 800°C.²⁴ Large, centimeter size, single crystals of BaMgF₄ have been grown by Czochralski and Bridgeman methods. In these reports either CF₄ or anhydrous HF gas was used at ~ 920°C.²⁵⁻²⁷ Sol-gel methods to synthesize polycrystalline BaMgF₄ have also been reported, however, in these reports BaF₂ and/or MgF₂ impurities were found.²⁸⁻²⁹ To date, there are no published reports on the bulk, polycrystalline, *pure-phase* syntheses of the BaMF₄ family of materials. Such syntheses would aid in growing high quality films of these materials, as the pure bulk materials could be used as an ablation target. We synthesized, for the first time, *pure and polycrystalline* BaMF₄ (M =

Mg, Mn, Co, Ni, and Zn) through a convenient low temperature hydrothermal route.

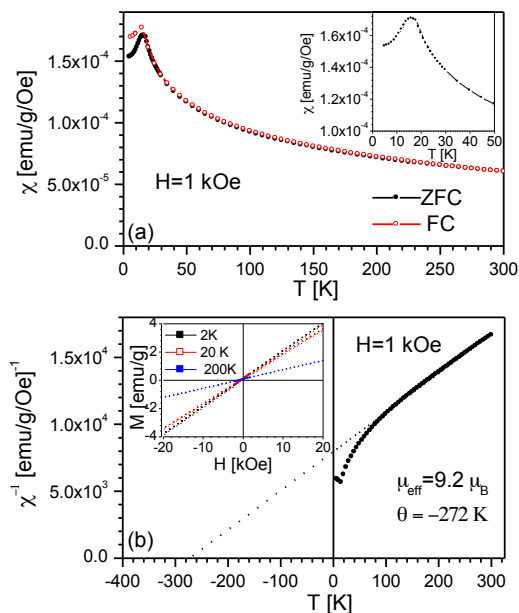
All of the materials were synthesized by combining the reagents into separate 23 ml autoclaves. The autoclaves were closed, heated to 230°C, held for 24h, and cooled slowly to room temperature at 6 °C h⁻¹. The mother liquor was decanted from the products, and the products were recovered by filtration and washed with distilled water. All of the reported materials, BaMF₄ (M = Mg, Mn, Co, Ni, and Zn) were synthesized as phase-pure polycrystalline powders. Additionally, magnetic measurements were performed on BaNiF₄ to confirm the magnetic ordering. As seen in the figure below, an anti-ferromagnetic transition at ~60K is observed, consistent with previous reports. With our hydrothermal method, we were also able to grow crystallographic quality crystals of BaMnF₄, BaCoF₄, and BiNiF₄.

In summary, we have discovered a convenient hydrothermal route for the low temperature and high yield phase-pure synthesis of the multi-ferroic family BaMF₄ (M = Mg, Mn, Co, Ni or Zn). The method avoids the use of HF by using a milder fluorinating agent, CF₃COOH, in an aqueous medium. The reported method provides a mild route for the bulk synthesis of these multi-ferroic materials, and ultimately may be used toward the development of targets for thin film growth. We are continuing our hydrothermal efforts using CF₃COOH towards the synthesis of other mixed-metal fluorides.

(ii) RbFe₂F₆ – A New Charge Ordered Magnetically Frustrated Mixed-Metal Oxide:

Utilizing the hydrothermal method developed for the synthesis of the BaMF₄ family of materials, we have synthesized a new charge ordered magnetically frustrated material – RbFe₂F₆ (RbFe(II)Fe(III)F₆). RbFe₂F₆ was obtained by hydrothermal methods using a diluted CF₃COOH solution. RbFe₂F₆ exhibits a three-dimensional crystal structure consisting of corner-shared FeF₆ octahedra that are separated by Rb⁺ cations (see Figures below). The formula may be also written as RbFe²⁺Fe³⁺F₆, as the Fe²⁺ and Fe³⁺ cations are ordered in the structure. The structure of RbFe₂F₆ may be described as being built up from two connected FeF₆ octahedral sub-lattices. These Fe³⁺F₆ chains are connected through Fe²⁺F₆ octahedra along the c-axis direction. Similarly, chains of Fe²⁺F₆ octahedra share corners along the a-axis direction, and these chains are connected through Fe³⁺F₆ octahedra along the c-axis direction.

Considerable additional information can be gathered from the χ^1 vs. T plot shown in the Figure. The data are seen to adhere rather well to the Curie-Weiss (C-W) form ($\chi = C/(T-\theta)$, where C and θ are constants), for $T > 100$ K or so, yielding an effective number of Bohr magnetons of $9.2 \mu_B$ / f.u., and a Weiss temperature of -272 K. Note that measurement of $\chi(T)$ in magnetic fields in the range 10^2 – 10^4 Oe yielded magnetic moment and θ values that varied by only about 10 %, consistent with the fact that the



$M(H)$ curves are quite linear at all T (see inset to Figure) The extracted values are similarly robust with respect to the exact temperature range used for the fitting to the C-W form. The theoretical spin only value is $5.42 \mu_B$ / Fe attributable to the equal contribution of the Fe^{2+} ($\mu_{\text{eff}} = 4.9 \mu_B$) and Fe^{3+} ($\mu_{\text{eff}} = 5.9 \mu_B$) cations. The difference between the theoretical and experimental values may be associated with short-range ordering that is observed at 250 K in the neutron diffraction data. Importantly, the -272 K Weiss temperature indicates relatively strong AF interactions between the Fe moments. In fact, comparison to the actual AF ordering temperature of 16 K indicates significant magnetic frustration in this compound, with a frustration ratio (θ / T_N) of 17.

(iii) **CsSnF₃ – A Rare Example of a Mixed-Metal Sn(II) Fluoride**

CsSnF₃ was synthesized by solvothermal techniques using methanol as a solvent. CsSnF₃ exhibits a ‘zero-dimensional’ structure with isolated SnF_3^- anionic polyhedra separated by Cs^+ cations (see Figure 1). The Sn^{2+} cation is bonded to three fluorine ligands, with Sn–F bond distances ranging from 2.0201(18) – 2.0560(19) Å. The Cs^+ cation is in a ten-fold coordination environment with Cs–F distances between 2.9903(18) – 3.7574(18) Å. Bond valence sum calculations resulted in values of 0.98, 2.22 and 0.976 – 1.16 for Cs^+ , Sn^{2+} and F^- , respectively (see Table 4).¹⁻² Each Sn^{2+} cation is bonded to three fluorine atoms in distorted trigonal pyramidal coordination environment attributable to its stereo-active lone-pair. The asymmetric coordination environment of Sn^{2+} is polar, i.e., the SnF_3^- polyhedron exhibits a dipole moment. Dipole moment calculations using a

method described previously resulted in a value of 5.7 Debye for a SnF_3^- polyhedron. The lone-pairs on the SnF_3^- polyhedra are directed towards the empty channels in an anti-parallel manner, that results in the cancelation of individual dipole moments. Thus CsSnF_3 is macroscopically not polar.

Perovskite-like tilting: Although CsSnF_3 exhibits the perovskite ABX_3 formula, the structure of CsSnF_3 is clearly non-perovskite. Nonetheless, by expanding the Sn(II) coordination environment to five and including the stereo-active lone-pair, we are able to create a pseudo-octahedral environment for the Sn(II) cation (see Figure 2). In doing so, we are able to describe the SnF_5E octahedra (E is the stereo-active lone-pair) using the well-known perovskite tilting formalism. The octahedral tilts for the Sn(II) cation can be described as $a^+b^-c^-$.

The fundamental question we have been addressing is why does CsSnF_3 form in the structure observed by our experimental collaborators. To tackle this challenge we initiated a comparative first-principles study of CsSnF_3 , CsSrF_3 , and CsPbF_3 , in perovskite, distorted perovskites, and in CsSnF_3 structure type discussed above. Previously published structural studies for CsSrF_3 have indicated that it forms in the cubic perovskite $\text{Pm}\bar{3}\text{m}$ structure at room temperature. As far as we now, no low temperature studies have been reported. CsPbF_3 however was synthesized in 2001 by Berastegui and co-workers and reported as a rhombohedral polar perovskite, in the $\text{R}\bar{3}\text{c}$ space group below 187 K.ⁱ In the perovskite structure the Goldschmidt tolerance factors calculated from Brese's bond valence parametersⁱⁱ are 1.00, 0.95, and 0.94, respectively. All structural relaxations, phonon calculations, and self-consistent energy calculations were performed using VASP, a widely used first-principles simulation package.

The lowest energy perovskite structures for CsSnF_3 , CsPbF_3 , and CsSrF_3 are in the space groups P2_1 , $\text{R}\bar{3}\text{c}$,[†] and I4/mcm , respectively. We see that in the case of CsSnF_3 , the Halasyamani structure will dominate over the lowest-energy perovskite, but in the other two compounds, the perovskites are more energetically favorable.

e. Papers

1. 'Selective Pure-Phase Synthesis of the Multiferroic $BaMF_4$ ($M = Mg, Mn, Co, Ni$, and Zn) Family', J. Am. Chem. Soc., **2010**, 132, 17684-17685.
2. ' $RbFe^{2+}Fe^{3+}F_6$: Synthesis, structure, and characterization of a new charge-ordered magnetically frustrated pyrochlore-related mixed-metal fluoride', Chem. Sci., **2012**, 3, 741-751.
3. Synthesis and Characterization of $ASnF_3$ ($A = Na^+, K^+, Cs^+$), J. Solid State Chem., **2014**, 210, 213-218.
4. Interplay of Octahedral Rotations and Lone Pair Ferroelectricity in $CsPbF_3$, Inorg. Chem., **2015**, 54, 8536-8543.

f. People working on the Project

University of Houston: Weiguo Zhang (Post-doctoral Associate: 100%); Elise Pachoud (Post-doctoral Associate: 100%); Sun Woo Kim (Graduate Student: 100%)

Cornell University: Hena Das (Post-doctoral Associate: 50%); Eva Smith (Graduate Student: 100%)

