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Selective Pure-Phase Synthesis of the Multiferroic $BaMF_4$ (M = Mg, Mn, Co, Ni, and Zn) Family

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Abstract: A low temperature, high yield hydrothermal route has been discovered for the phase-pure synthesis of the multiferroic $BaMF_4$ (M = Mg, Mn, Co, Ni, and Zn) family. The synthesis involves the use of CF_3COOH instead of HF in an aqueous medium and, under the correct conditions, produces pure and polycrystalline $BaMF_4$. In addition to the synthetic description, second-harmonic generation, thermogravimetric, and differential scanning calorimetry data are presented.

Multiferroic materials, compounds where at least two primary ferroic — ferroelectric, ferromagnetic, ferroelastic, etc. — properties occur in the same materials, are of topical interest attributable to their applications in advanced devices.[1−3] With such materials, the magnetic properties may be controlled by an electric field and vice versa. A great deal of effort is dedicated to to not only discovering new multiferroic materials, e.g., $MnWO_4$[4−6] and Ca_3CoMnO_6,[7,8] but also investigating multiferroic behavior in known materials, e.g., $BiFeO_3$.[9−16] A family of materials that has received renewed interest are the mixed-metal fluorides $BaMF_4$ (M = Mg, Mn, Fe, Co, Ni, and Zn).[17−21] These iso-structural and crystallographically polar materials — all of the materials crystallize in the polar space group $Cmc2_1$ — are ferroelectric at room temperature for M = Mg, Co, Ni, and Zn[22] and exhibit antiferromagnetic ordering with $T_N \approx$ 20−80 K for M = Mn, Fe, Co, and Ni.[23] Thus simultaneous ferroelectric *and* antiferromagnetic behavior, at low temperatures, may only be observed in $BaCoF_4$ and $BaNiF_4$.

Originally, the $BaMF_4$ family of materials were grown as crystals from the melt of BaF_2 and MF_2 in an HF atmosphere at elevated temperatures — above 800 °C.[24] Large, centimeter size, single crystals of $BaMgF_4$ have been grown by Czochralski and Bridgeman methods. In these reports either CF_4 or anhydrous HF gas was used at ∼920 °C.[25−27] Sol−gel methods to synthesize polycrystalline $BaMgF_4$ have also been reported; however, in these reports BaF_2 and/or MgF_2 impurities were found.[28,29] To date, there are no published reports on the bulk, polycrystalline, *pure-phase* syntheses of the $BaMF_4$ 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. In this communication, we report on the synthesis of *pure and polycrystalline* $BaMF_4$ (M = Mg, Mn, Co, Ni, and Zn) through a convenient low temperature hydrothermal route.

All of the materials were synthesized by combining the reagents (see Table 1) into separate 23 mL autoclaves. The autoclaves were closed, heated to 230 °C, held for 24 h, 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. Reagent ratios used were as follows (see Supporting Information, S1, for complete details regarding the synthetic procedure).

Table 1. Reagent Amounts and Yields for the Synthesis of $BaMF_4$ (M = Mg, Mn, Co, Ni, and Zn)

	$BaMgF_4$	$BaMnF_4$	$BaCoF_4$	$BaNiF_4$	$BaZnF_4$
BaF_2	0.187 g	0.200 g	0.150 g	0.100 g	0.180 g
MF_2	0.245 g[a]	0.106 g	0.110 g	0.385 g[b]	0.351 g[b]
CF_3COOH	4 mL	2 mL	3 mL	5 mL	4 mL
H_2O	5 mL	5 mL	5 mL	5 mL	5 mL
Yield[c]	70%	80%	70%	80%	80%

[a] For $BaMgF_4$, $Mg(ac)_2{\cdot}4H_2O$ was used. [b] For $BaNiF_4$ and $BaZnF_4$, $MF_2{\cdot}4H_2O$ was used. [c] Yields based on BaF_2.

All of the reported materials, $BaMF_4$ (M = Mg, Mn, Co, Ni, and Zn), were synthesized as phase-pure polycrystalline powders. Experimental and calculated X-ray diffraction (XRD) data for $BaNiF_4$ are shown below (see Figure 1). Powder XRD data for the other reported phases have been deposited in the Supporting Information (see Figure S2).

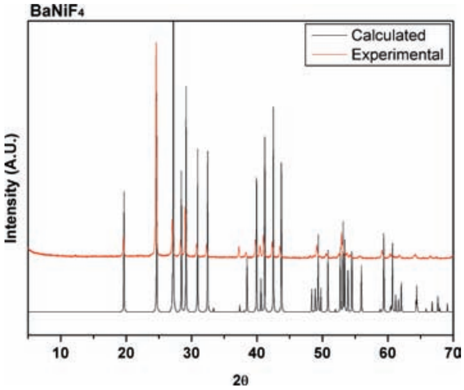

Figure 1. Calculated (black) and experimental (red) powder X-ray diffraction data for $BaNiF_4$.

Additionally, magnetic measurements were performed on $BaNiF_4$ to confirm the magnetic ordering. As seen in Figure S3, an antiferromagnetic transition at ∼60 K is observed, consistent with previous reports.[23] With our hydrothermal method, we were also able to grow crystallographic quality crystals of $BaMnF_4$, $BaCoF_4$, and $BiNiF_4$. Crystallographic information for these three materials have been included in the Supporting Information. The structures are consistent with previous reports (see Table S4). Briefly, $BaMF_4$ (M = Mg, Mn, Co, Ni, and Zn) represent an iso-structural family of materials that contain layers of corner-shared MF_6 octahedra that are separated by Ba^{2+} cations (see Figure 2). The M−F bond distances, for $BaMnF_4$, $BaCoF_4$, and $BiNiF_4$, range from 1.981(9) to 2.159(5) Å, with Ba−F distances of 2.611(5)−3.355(5) Å. Bond valence calculations[30,31] resulted in values ranging from 1.85 to 2.02 for the Ba^{2+} cation and 1.95, 1.99, and 2.00 for Mn^{2+}, Co^{2+}, and Ni^{2+}, respectively. In connectivity terms, the structures may

10.1021/ja108965s

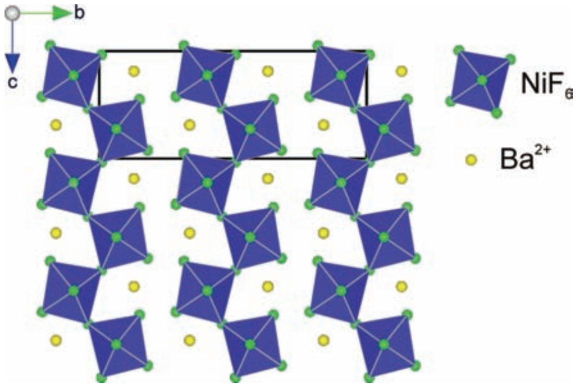

Figure 2. Polyhedral diagram of $BaNiF_4$ in the *bc*-plane.

be written as $[MF_{4/2}F_{2/1}]^{2-}$ with the charge balance retained by the Ba^{2+} cations.

Functional property characterization of the $BaMF_4$ family has been reported. These include ferroelectric,[22] piezoelectric,[24] nonlinear optical,[32] magnetic,[23] and neutron diffraction measurements.[19] More recently a first principles study on the origin of the ferroelectric behavior has been reported.[21] We performed powder second-harmonic generating (SHG) measurements on the reported materials and determined that all of the materials as type 1 phase-matchable with an SHG efficiency of approximately $2 \times \alpha\text{-}SiO_2$ (see Figure S5). This relatively weak SHG efficiency is not too surprising as there are no polarizable cations—octahedrally coordinated d^0 transition metals or lone-pair cations in the materials. Thermogravimetric measurements indicated that $BaMF_4$ is thermally stable up to 550 °C under N_2 (see Figure S6). Above this temperature, the materials decompose to BaF_2 and other mixed-metal fluorides (see Figure S7). $BaMF_4$ materials are stable above 750 °C in both gaseous HF and CF_4 atmospheres;[25−27] however under N_2 the materials decompose above 550 °C. Differential scanning calorimetry measurements on all of the reported materials revealed no phase changes up to 500 °C (see Figure S8). Infrared data revealed ν_{M-F} stretches (M = Mg, Mn, Co, Ni or Zn) between 624 and 425 cm^{-1} and ν_{Ba-F} vibrations between 427 and 409 cm^{-1} (see Figure S9). These assignments are consistent with previous reports.[33]

In summary, we have discovered a convenient hydrothermal route for the low temperature and high yield phase-pure synthesis of the multiferroic family $BaMF_4$ (M = Mg, Mn, Co, Ni or Zn). The method avoids the use of HF by using a milder fluorinating agent, CF_3COOH, in an aqueous medium. The reported method provides a mild route for the bulk synthesis of these multiferroic materials and, ultimately, may be used toward the development of targets for thin film growth. We are continuing our hydrothermal efforts using CF_3COOH toward the synthesis of other mixed-metal fluorides.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant E-1457) and the DOE-BES (DE-SC0005032) for support. We also thank Dr. Michael Hayward (University of Oxford, U.K.) for the magnetic measurements on $BaNiF_4$.

Supporting Information Available: The complete synthetic procedure, powder X-ray diffraction, magnetic susceptibility, single crystal (cif), powder second-harmonic generation, thermogravimetric, differential scanning calorimetry, and infrared spectroscopy data are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA108965S