SUPPLEMENTARY INFO

Structure-property trends in a hollandite multiferroic by Fe doping: Structural, magnetic and dielectric characterization of nanocrystalline Ba $Mn_{3-x}Fe_xTi_4O_{14+\delta}$

Frederick Pearsall,^{a,b,c} Nasim Farahmand, ^{a,b,c} Julien Lombardi^{a,b,c}, Sunil Dehipawala^d, Zheng Gai^e and Stephen O'Brien^{a,b,c*}

^aThe CUNY Energy Institute, City University of New York, Steinman Hall, 160 Convent Avenue, The City College of New York, New York, NY 10031, USA.

^bDepartment of Chemistry, The City College of New York, 1024 Marshak, 160 Convent Avenue, NY 10031, USA

° Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, NY 10016, USA.

^dDepartment of Physics, Queensborough Community College, 222-05 56th Ave, Bayside, New York, NY 11364, USA

^eCenter for Nanophase Materials Sciences and Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Keywords: multiferroic, nanoscale, Mossbauer spectroscopy, magnetic, dielectric

*Corresponding author: sobrien@ccny.cuny.edu



Figure S1. (a), (b) show the gel-rod obtained after the gel-collection synthesis as well as the nanopowder obtained after heat treatment, respectively. Fig S1 (c) pellet press used to press the BMFT powder pellets. Fig. S1 (d) metal-insulator-metal (MIM) capacitors made from the pressed pellets and conductive silver epoxy.

Figure S2. Effective permittivity vs frequency and impedance analysis for the series of BMFT samples (0:1 to to 3:1). Frequency range is 100 Hz to 2 MHz. (a) Effective permittivity vs frequency; (b) dissipation factor (tan δ) vs frequency. See also Figure 5 in article for conductivity.



Structural Characterization and Elemental Analysis of BMFT

Figure S3. (a) is a TEM micrograph of BMFT nanoparticles. The particles range from 100 - 300 nm. Fig. S3 (b) shows an SEM micrograph of a pressed pellet of BMFT (no further sintering), showing a more detailed morphology for the particles. 3-dimensional void space is clearly visible in Fig. S3 (b).



Inspection of Bragg peak locations from the powder X-ray diffraction pattern. Three planes, corresponding to Miller indices (220), (310) and (420), (Fig. S4, S5 and S6 respectively) were chosen for analysis as the number of Ba ions and metal octahedra which are bisected by these planes vary. For example, the (220) and (310) planes give rise to Bragg peaks whose intensity is predominantly dependent upon barium ion. The (420) plane bisects the center of Ti octahedra and partially cuts the Mn and Fe octahedra.



Fig. S4 (a) demonstrates the only cation the (220) plane intersects is Ba^{2+} . Fig. S4 (b) shows an overall decrease in lattice spacing for replacing Mn. This suggests a change in the surrounding octahedra that may cause a shrinking of the distance between barium ions in this plane. Fig. S5 (a) illustrates that Ba ions as well as some metal octahedra are bisected by the (310) plane. The decrease in d spacing for the plane observed in Fig. S5 b) is much less than that for the (220) plane, due to its intersection with more ions and

octahedra. Fig. S5 a) is of the (420) lattice plane. This plane bisects the centers of titanium octahedra. Its decrease in d spacing is also much less than that for the (220) plane, as can be seen in Fig. S6 (b).



due to the intersection with more barium ions. It can be seen for all cases that the 3:1 ratio compound does not follow the trend for changes in lattice distance. It tends to either decrease *less* or, in the case of Fig. S5 (b), *increase* rather than decrease. It may be that a critical ratio of Fe:Mn is required in order to retain the hollandite crystal structure, as the compound accommodates for the increased Fe.



Energy dispersive X-ray spectroscopy was used to verify the elements present within the BMFT crystals. Neglecting the oxygen content, the total ratio of iron and manganese are estimated. EDS values derived from the JEOL software is not a very accurate quantitative indicator for elemental analysis in this case but clearly shows the trend of increasing Fe and Fe:Mn ratio. The accuracy of the EDS is most likely much less than that of synthesis procedure, and therefore these values serve as a guide as opposed to any concrete determination, and show the general trend of increasing Fe:Mn ratio within a satisfactory error margin.

Element	BaMn ₂ FeTi ₄ O _{14+δ}	BaMn _{1.5} Fe _{1.5} Ti ₄ O ₁₄	BaMnFe ₂ Ti ₄ O _{14+δ}
Atomic %			
Ti	19.24	19.57	34.48
Mn	7.22	5.19	7.27
Fe	2.89	5.39	11.87
Ba	4.81	6.23	8.75
Calculated Mn:Fe ratio	2.4:1	0.95:1	0.6:1
Expected Mn:Fe ratio	2:1	1:1	0.5:1

Table S1. Atomic % of the BMFT crystal variants obtained from EDS.

Fe:Mn	Permittivity at 1 MHz
3:1	110
2:1	138
1:1	157
1:2	167
0:1	206

Table S2. Impedance analysis: effective permittivity at 1 MHz



Figure S7. Resistivity vs log frequency plot from Impedance spectroscopy.