

# Search for Displacive-type Multiferroics with a Huge Magnetoelectric Coupling

B. Dabrowski<sup>1</sup>, Kolesnik<sup>1</sup>, J. Mais<sup>1</sup>, O. Chmaissem<sup>1</sup>, S. V. Goian<sup>2</sup>,  
S. Kamba<sup>2</sup>,

<sup>1</sup>Department of Physics, Northern Illinois University, DeKalb, IL, USA,

<sup>2</sup>Institute of Physics, Academy of Sciences of the Czech Republic

It has been recently proposed [1-3] that it should be possible to introduce ferromagnetism and ferroelectricity in  $\text{Sr}^{2+}\text{Mn}^{4+}\text{O}_3$  and derivative materials when tensile strains up to 4.9% are achieved. These compounds were predicted to exhibit huge spontaneous polarizations  $P_s > 54 \text{ mC/cm}^2$  and  $T_C > 92 \text{ K}$ . We have been working with similar manganites for two decades and projected earlier that similar to the  $d^0$  titanates [4,5] strain effects should be observed in the non- $d^0$  perovskites resulting in a strong ferroelectric-magnetic coupling of the same magnetic ion.[6,7] However, until only recently, it was proven challenging to achieve the displacive ferroelectric distortion in the  $d^3$  manganites because the  $[\text{Mn}^{4+}\text{-O}]$  bonds have not been put under sufficient tension.[8] By advancing elaborate synthesis processes, which are necessary to avoid the more stable hexagonal polymorphs, we were recently able to extend the substitution limit of the large size Ba ion in bulk  $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$  samples to  $x = 0.45$  with two-step “*in situ*” synthesis in a thermogravimetric furnace in flowing  $\text{H}_2/\text{Ar}$  gas followed by oxygen anneal (Fig.1).[9,10] The achieved perovskite ceramics exhibit ferroelectricity ( $T_F > 300 \text{ K}$ ) and G-type antiferromagnetism ( $T_N \sim 200 \text{ K}$ ) originating exclusively from the Mn cations. Similar to  $\text{Ba}^{2+}\text{Ti}^{4+}\text{O}_3$ , the classical displacive-type ferroelectric phase transition occurs for  $x > 0.4$  when the Mn ions move out of the center of the  $\text{MnO}_6$  octahedral units. These materials show on cooling a sequence of transitions from the paramagnetic and paraelectric cubic phase to the paramagnetic and ferroelectric tetragonal  $P4mm$  phase and finally to antiferromagnetic and paraelectric  $P4/mmm$  phase. The largest known magneto-electric coupling was observed near  $T_N$  when ferroelectricity disappears. Our more recent efforts focus on Ti-substituted  $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$  materials since they show enhanced spontaneous polarizations at higher temperatures and a tunable suppression of displacive ferroelectric distortion by magnetic transition. I will describe our study of the  $(\text{Sr,Ba})(\text{Mn,Ti})\text{O}_3$  phase diagram in search of displacive-type multiferroic perovskites as well as improper hexagonal multiferroics. Our two-step synthesis methods can be also extended to other substituted systems with the elongated mixed-valent  $[\text{Mn}^{3/4+}\text{-O}]$  bonds as well as to other transition metals where new exciting properties should be found.

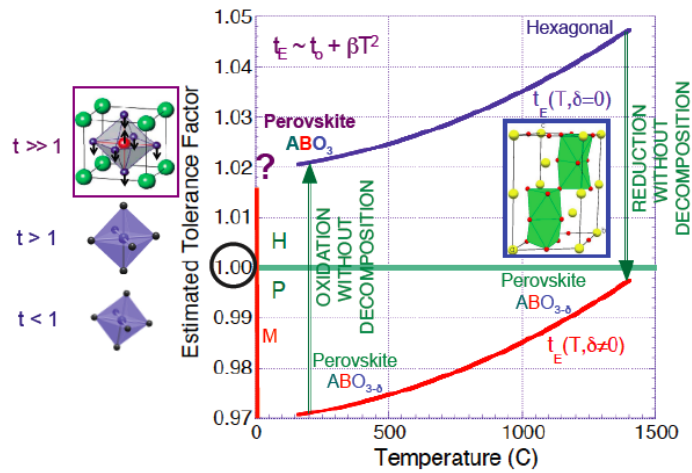


Fig.1 Figure 1 demonstrates schematically the idea used to achieve transition metal  $AMO_{3-\delta}$  perovskites by use of “tolerance factor synthesis-properties design rules”. [10] Relying on the simple tolerance factor  $t(x, T, \delta) = [A-O]/\sqrt{2}[M-O]$  defined as a function of chemical composition, temperature and oxygen nonstoichiometry of the  $[A-O]$  and  $[M-O]$  interatomic distances, our design rules describe a sequence of synthesis steps necessary to achieve perovskites with nominally  $t > 1$  around room temperature; i.e., with the  $[M-O]$  bonds put under severe internal tension.

## References

1. J.H. Lee and K.M. Rabe, Phys. Rev. Lett. 104, 207204-1-4 (2010)
2. S. Bhattacharjee, E. Bousquet, and P. Ghosez, Phys. Rev. Lett. 102, 117602-1-4 (2009)
3. J.M. Rondinelli, A.S. Eidelson, and N.A. Spaldin, Phys. Rev. B 79, 205119-1-6 (2009)
4. V.V. Lemanov, E.P. Smirnova, P.P. Syrnikov, and E.A. Tarakanov, Phys. Rev. B 54, 3151-3157 (1996)
5. M.A. Carpenter, C.J. Howard, K.S. Knight, and Z. Zhang, J. Phys.: Condens. Matter 18 10725–10749 (2006)
6. B. Dabrowski, O. Chmaissem, J. Mais, S. Kolesnik, J.D. Jorgensen, and S. Short, J. Solid State Chem. 170, 154-164 (2003)
7. O. Chmaissem, B. Dabrowski, S. Kolesnik, J. Mais, D.E. Brown, R. Kruk, P. Prior, B. Pyles, J.D. Jorgensen, Phys. Rev. B 64, 134412 (2001)
8. H. Sakai, J. Fujioka, T. Fukuda, D. Okuyama, D. Hashizume, F. Kagawa, H. Nakao, Y. Murakami, T. Arima, A.Q.R. Baron, Y. Taguchi, and Y. Tokura, Phys. Rev. Lett. 107, 137601 (2011)
9. D.K. Pratt, J.W. Lynn, J. Mais, O. Chmaissem, D.E. Brown, S. Kolesnik, and B. Dabrowski, Phys. Rev. B 90, 140401(R) (2014)
10. B. Dabrowski, O. Chmaissem, J. Mais, and S. Kolesnik, Acta Physica Polonica A 105, 45-56 (2004)