Multiferroic $Sr_{1-x}Ba_xMnO_3$ Perovskite with a Huge Magnetoelectric Coupling

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It has been recently proposed [1-3] that it should be possible to introduce ferromagnetism and ferroelectricity in $SrMnO_3$ and derivative materials when strains up to 4.9% are achieved, with a computed huge spontaneous polarization $P_s > 54$ mC/cm^2 and $T_C > 92$ K. We have also 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 $[Mn^{4+}-O]$ 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 extended the substitution limit of the large size Ba ion in bulk $Sr_{1-x}Ba_xMnO_3$ samples to $x = 0.45$ with "*in situ*" synthesis in a thermogravimetric furnace in flowing H_2/Ar gas.[9]

Figure 1 demonstrates schematically the idea used to achieve such 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; i.e., with the $[M-O]$ bonds put under severe internal tension.

The achieved perovskite ceramics (x = 0.4-0.45) exhibit ferroelectricity ($T_F > 300$ K) and G-type antiferromagnetism ($T_N \sim 200$ K) originating exclusively from the Mn cations. Similar to $Ba^{2+}Ti^{4+}O_3$, the classical displacive-type ferroelectric phase transition occurs for x > 0.4 when the Mn ions move out of the center of the 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. Because of high conductivity the measurements of complex dielectric permittivity are reliable only below 40 K, where intrinsic permittivity is about 340 and does not change with magnetic field up to 9 T. The antiferromagnetic order parameter has energy

gap of 4.6(5) meV and the top of the magnon band at 43(1) meV. Nearest-neighbor exchange modeling indicates exchange constant of J=4.8(2) meV.
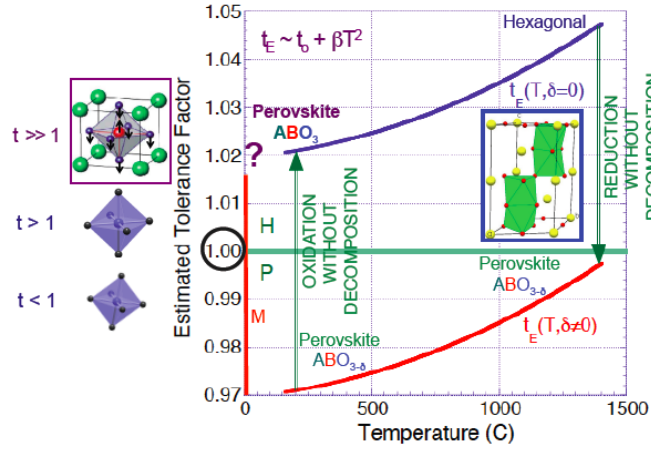

Fig.1 Schematic picture of utilization of properties of tolerance factor $t(x, T, \delta)$ to synthesize perovskites with t > 1 at room temperature.

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