Synthesis of the Mn-ion Based Perovskite Multiferroics

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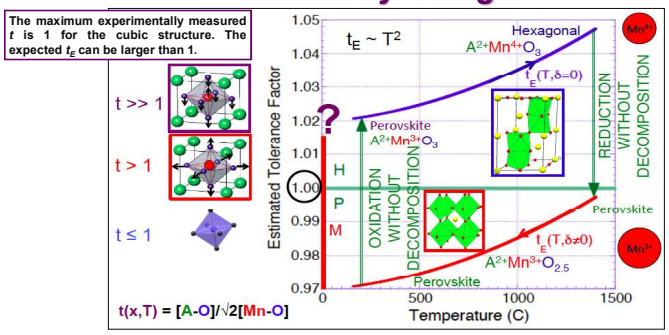
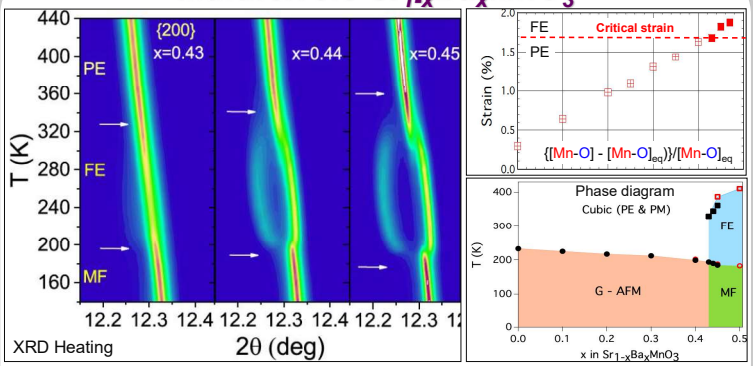
We have designed and synthesized manganese multiferroics $Sr_{1-x}Ba_xMn_{1-y}Ti_yO_3$ exhibiting ferroelectricity (FE) and magnetism originating solely from the Mn^{4+} (d^3) ion. The structural study show large FE-type distortions, which are reduced by antiferromagnetism indicating strong coupling. The Ti-substituted compounds have increased transition temperatures and larger derived FE polarizations than $BaTiO_3$. The scarcity of similar multiferroic systems is caused by the difficulty of obtaining compounds with expected tolerance factor $t_E > 1$ near the room temperature, and not due to the incompatibility of the magnetic systems with the FE (d^0) as suggested by the "d^0-ness conjecture" (Hill, J. Phys. Chem. B, 2000).

Materials by Design



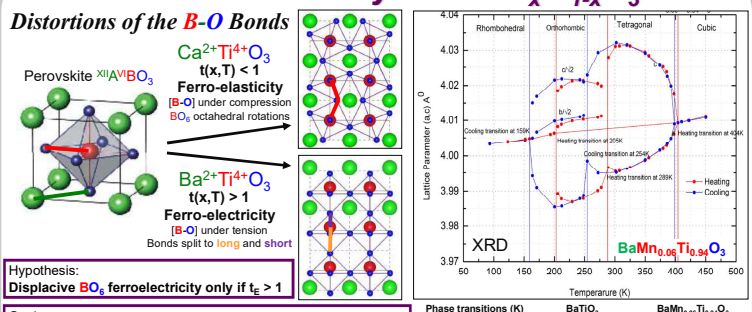
Two-step synthesis was used to remove hexagonal non-FE phase by: Reducing the oxygen content at high temperatures to form perovskite framework by decreasing the tolerance factor below putting back oxygen at low temperature by annealing.

Multiferroic $Sr_{1-x}Ba_xMnO_3$



Compositions x = 0.43 – 0.45 show multiferroic properties. The required elongation of the [Mn-O] bond is 1.7% to split it into long and short bonds along the c-axis.

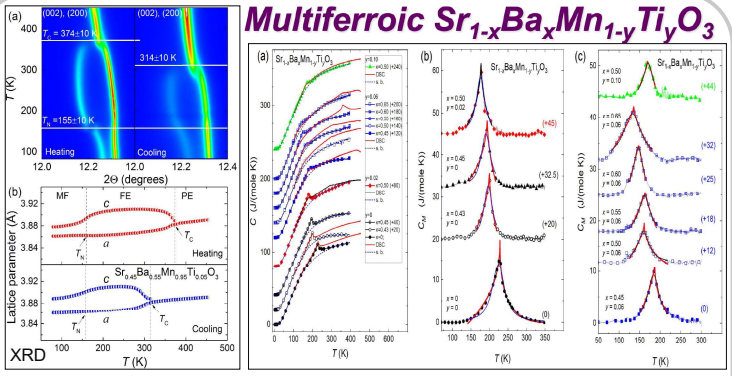
Ferroelectricity in $BaMn_xTi_{1-x}O_3$



Phase transitions (K)	$BaTiO_3$	$BaMn_{0.06}Ti_{0.94}O_3$
Cubic	401 - 394 = 7 K	404 - 398 = 6 K
Tetragonal	285 - 279 = 6 K	289 - 254 = 35 K
Orthorhombic	196 - 181 = 15 K	205 - 159 = 46 K

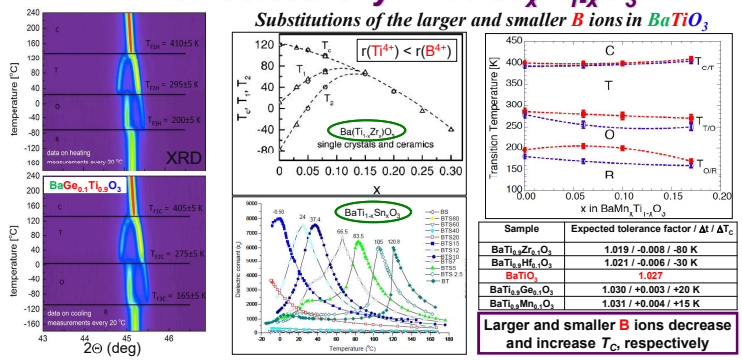
Increase of the C/T transition temperature is seen as predicted. The Mn-substitution preserves uniquely all ferroelectric transitions while increasing the *T*-hysteresis.

Multiferroic $Sr_{1-x}Ba_xMn_{1-y}Ti_yO_3$



The FE transitions show huge temperature hysteresis at T_C, an increased c/a ratio and T_C *to* 420 K, as well as reduced suppression of distortion at T_N. Specific heat studies show that AFM transition changes from the continuous to discontinuous.

Ferroelectricity in $BaGe_xTi_{1-x}O_3$



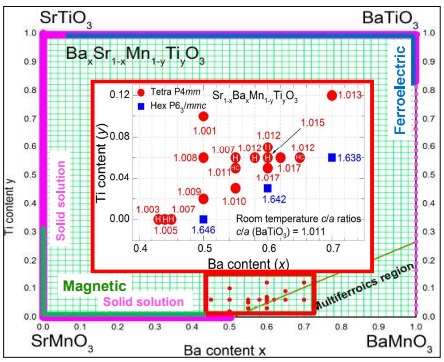
Sample	Expected tolerance factor / Δt / ΔT_C
$BaTi_{0.9}Zr_{0.1}O_3$	1.019 / -0.008 / -80 K
$BaTi_{0.9}Hf_{0.1}O_3$	1.021 / -0.006 / -30 K
$BaTiO_3$	1.027
$BaTi_{0.9}Ge_{0.1}O_3$	1.030 / +0.003 / +20 K
$BaTi_{0.9}Mn_{0.1}O_3$	1.031 / +0.004 / +15 K

Larger and smaller B ions decrease and increase T_C, respectively

Prediction of increasing T_C by increase of the [B-O] bond tension was verified. Established the essential parameter for displacive ferroelectricity: $t_E(x,T) > 1$

Why So Few Magnetic Ferroelectrics Exist?

The reason for the scarcity of similar multiferroic systems is caused by the difficulty of obtaining compounds with expected tolerance factor $t_E > 1$. This is due to usual demands of the synthesis conditions of t < 1 to form the perovskite at high temperatures and their universal dependence of decreasing t(T) with lowering temperature. These problems have been removed by the two-step synthesis procedure.



We have achieved the FE distortions in magnetic perovskites $Sr_{1-x}Ba_xMn_{1-y}Ti_yO_3$ when the Mn-O bonds were stretched beyond equilibrium lengths.

The two-step synthesis, which uses chemical pressure instead of hydrostatic pressure provides a method to synthesize the large size samples of novel compounds for multivalent transition and rare earth metals with varying ionic sizes. We have used the method to stabilize as well as to destabilize several perovskites and non-perovskites for basic studies and application.

Supported by the Polish NCN through Grant No. 2018/31/B/ST5/03024

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