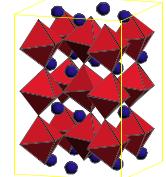


# Design Rules for New Manganite Compounds with Novel Magnetic and Electronic Properties

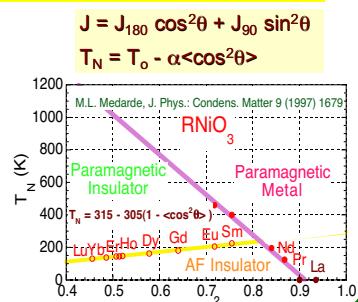
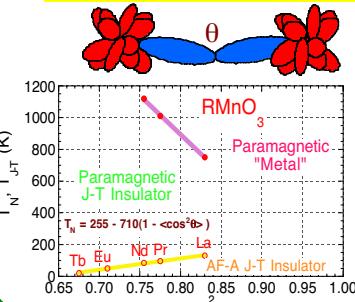
B. Dabrowski, O. Chmaissem, Northern Illinois University and Argonne National Laboratory; J. D. Jorgensen, E. Caspi, S. Short, Argonne National Laboratory; J. Mais, S. Kolesnik, Northern Illinois University

**Motivation:** Perovskite compounds  $\text{ABO}_3-\delta$  display a broad range of magnetic, electronic, ferroelectric, and ionic conductivity behavior depending on the chemical composition and crystal structure. To utilize these materials in applications, we have been systematically developing "design rules" for controlling the properties by special synthesis techniques for extending chemical composition ranges, establishing rules for predicting what compositions it should be possible to make, and developing methods for selectively ordering or disordering mixtures of metal atoms on the A or B sites.

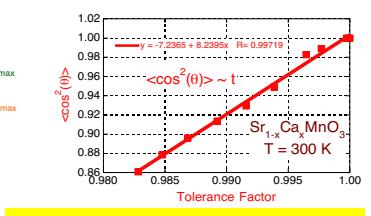
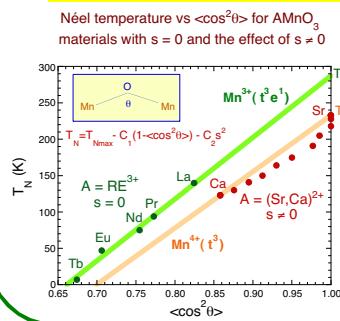


Crystal Structure of  $\text{ABO}_3$

## Dependence of the AFM interactions and Néel temperature on the B - O - B Bond Angle

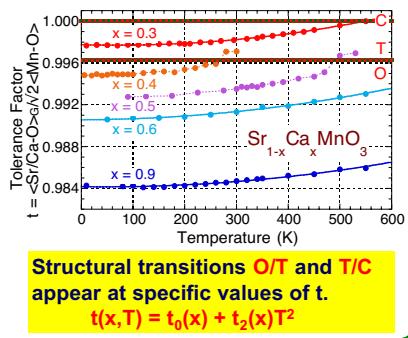
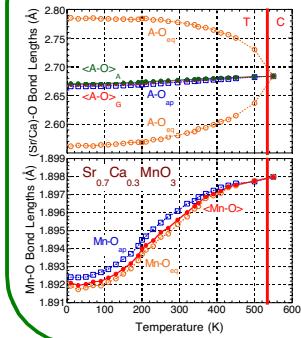


## Dependence of Néel temperature on $\cos(\theta)$ , tolerance factor $t$ , and variance of sizes $s$



Maximum  $T_N$ 's are found for straight Mn-O-Mn bonds ( $\cos(\theta) \sim 1$ ) and minimal variance of sizes ( $s=0$ )

## Temperature dependence of structural parameters

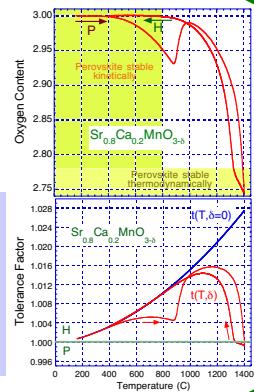


Structural transitions O/T and T/C appear at specific values of  $t$ .  
 $t(x,T) = t_0(x) + t_2(x)T^2$

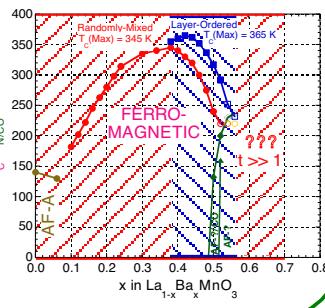
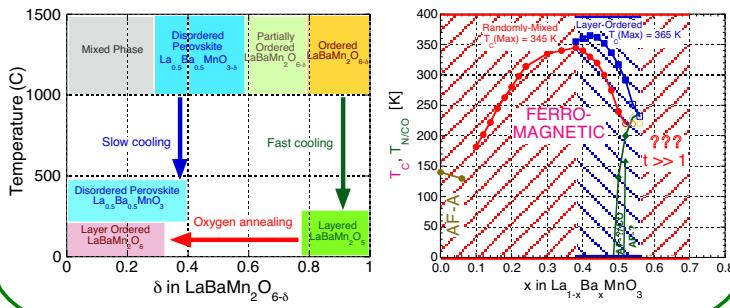
## Tolerance factor and stability of the perovskite structure

How is it possible to synthesize  $\text{AMnO}_3$  perovskites with  $t = [\text{A}-\text{O}] / \sqrt{2[\text{B}-\text{O}]} > 1$ ?

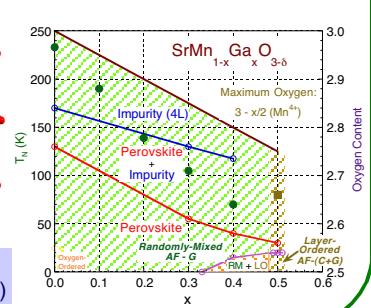
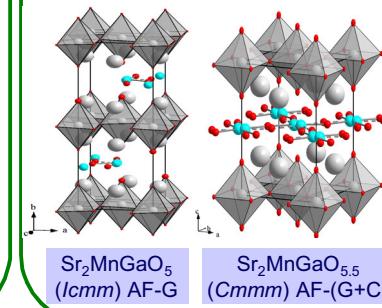
[ $\text{Mn}^{3+}-\text{O}$ ] is larger than [ $\text{Mn}^{4+}-\text{O}$ ]  
--  $t(\delta)$  decreases with increasing oxygen-vacancy content  
-- remove oxygen while doing the initial synthesis at high temperature  
-- reinsert the oxygen at a lower temperature where decomposition cannot occur



## Increase of $T_c$ for A-site layer-ordered $\text{La}_{1+x}\text{Ba}_{1-x}\text{Mn}_2\text{O}_6$ perovskites

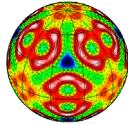


## Properties of B-site randomly-mixed and layer-ordered perovskites $\text{SrMn}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$



**Impact:** Our design rules for the synthesis of perovskites enable the compositions and crystal structures of these materials to be controlled in order to achieve the desired physical and chemical properties for applications.

**Tolerance Factor Rules for  $\text{Sr}_{1-x-y}\text{Ca}_y\text{Ba}_x\text{MnO}_3$  Perovskites.** B. Dabrowski, O. Chmaissem, J. Mais, S. Kolesnik, J. D. Jorgensen, and S. Short, *J. Solid State Chem.* 170, 154 (2003)



BES - DOE

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MSD - ANL

