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Evan Smith
Boise State University

Kevin Tolman
Boise State University

Rick Ubic
Boise State University

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The electroceramics industry largely relies on various time-consuming and expensive trial-and-error experiments to address new questions which often could otherwise be interpolated from published data. Towards this end, predictive models, which can be derived from empirical evidence, can greatly aid the direction of future development in a meaningful and cost-effective way. This work focuses on deriving predictive models based on empirical data collected for ceramic compounds with the perovskite crystal structure. Specifically, models were made for layered type ordering in the $[(Na_yLi_{1-y})_{(1-3x)/2}La_{(1+x)/2}]TiO_3$ system and rocksalt ordering in $Ba(Mg_{⅓}Ta_{⅔})O_3$.

BOISE STATE UNIVERSITY

COLLEGE OF ENGINEERING

MICRON SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

Empirical Modeling of Cation Ordering in Perovskite Ceramics

Evan Smith, Kevin Tolman,* Rick Ubic

Micron School of Materials Science and Engineering, Boise State University

* Current address: Idaho National Laboratory

Abstract

The electroceramics industry largely relies on various time-consuming and expensive trial-and-error experiments to address new questions which often could otherwise be interpolated from published data. Towards this end, predictive models, which can be derived from empirical evidence, can greatly aid the direction of future development in a meaningful and cost-effective way. This work focuses on deriving predictive models based on empirical data collected for ceramic compounds with the perovskite crystal structure. Theory suggests that intrinsic properties on the scale of a unit cell may be estimated from the sizes and charges of the chemical constituents alone. Ultimately, researchers could be provided a compositional recipe for some desired structure/property; or the resulting structure/property could be readily calculated based on composition. Empirical models also lend themselves to the exploration of structure/property trends which would otherwise be virtually impossible to discover via computationally expensive first-principles methods. In this work, models were made for layered ordering in the $[(Na_yLi_{1-y})_{(1-3x)/2}La_{(1+x)/2}]TiO_3$ (NLLT) system and rocksalt ordering in $Ba(Mg_{⅓}Ta_{⅔})O_3$ (BMT).

Perovskites

The term "perovskite" defines a particular crystal structure shown in figure 1. The A and B cations and X anions are located at the corners, body center, and face centers, respectively; and anion octahedra are corner-shared. Even when deformed and noncubic, a *pseudo*cubic lattice constant can be derived in several ways:

$$a_{pc} = \left(\frac{V}{Z}\right)^{1/3}$$

$$\longleftrightarrow a'_{pc} = \sqrt{2}(r_A + r_X)$$

$$\Longleftrightarrow a''_{pc} = 2(r_B + r_X)$$

where V = unit-cell volume; Z is the number of ABX_3 formula units per unit cell; and r_A, r_B, and r_X are the effective radii of A, B, and X species, respectively.

Figure 1: Perovskite crystal structure with arrows indicating the derivation of a' (black) and a'' (orange)

Results

B-site ordering data from $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) are presented in figures 8-9. A-site ordering data from $(Na_yLi_{1-y})_{(1-3x)/4}La_{(1+x)/2}TiO_3$ (NLLT) are presented in figures 10-12.

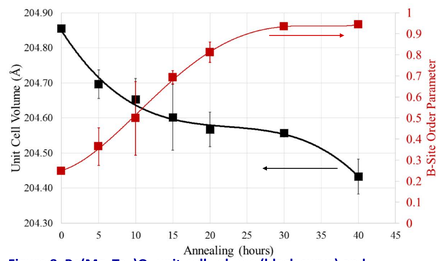

Figure 8: $Ba(Mg_{⅓}Ta_{⅔})O_3$ unit-cell volume (black curve) and order parameter (red curve) as a function of annealing time, t.

1.) $Vol = 204.85 - 0.0332t + 0.0014t^2 - 2x10^{-5}t^3 \quad (R^2 = 0.9917)$

3.) $\eta = \dfrac{0.973062}{1+\exp\left(\dfrac{8.72456-t}{7.37166}\right)} \quad (R^2 = 0.9989)$

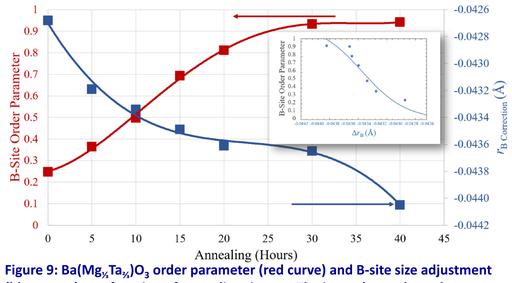

Figure 9: $Ba(Mg_{⅓}Ta_{⅔})O_3$ order parameter (red curve) and B-site size adjustment (blue curve) as a function of annealing time, t. The inset shows the order parameter as a function of Δr_B and can be thought of as an empirical model for ordering (0 = disorder, 1 = fully ordered).

2.) $\Delta r_B = -0.0427 - 0.0001t + 5x10^{-6}t^2 - 7x10^{-8}t^3 \quad (R^2 = 0.9952)$

4.) $\eta = \dfrac{1.22869}{1+\exp\left(\dfrac{0.0434304+\Delta r_B}{3.83894x10^{-4}}\right)}$

As Fig. 8 shows, increased rocksalt ordering on the B site is directly related to a **volume contraction**. The final volume can be calculated as a function of t (Eq. 1). The model developed[1,3] assumes a *disordered* structure, so a volume contraction requires a negative Δr_B term (Eq. 2) which modifies the effective B-site ionic size, r_B (Fig. 9). The order parameter, η, can now be calculated as a function of either annealing time, t (Eq. 3), or Δr_B (Eq. 4).

In the case of layered ordering on the A site, Figs. 10 and 11 show that increased ordering results in a **volume expansion**, requiring a positive Δr_A term. Eq. 5 describes this effect; and the *a*, *b*, and *c* terms are determined by the blue curves in Fig. 12. Eq. 6 describes η as a function of Δr_A where *A*, *B*, and *C* are determined by the red curves in Fig. 12. Both volume expansion and contraction can be explained in terms of crystal chemistry.

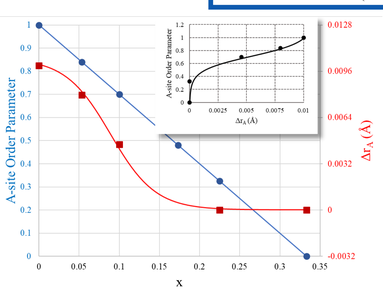

Figure 10: $Na_{(1-3x)/2}La_{(1+x)/2}TiO_3$ ordering from experimental site occupancies. Inset shows the order parameter as a function of Δr_A (Å) and can be thought of as an empirical model for ordering (0=disordered, 1=fully ordered).

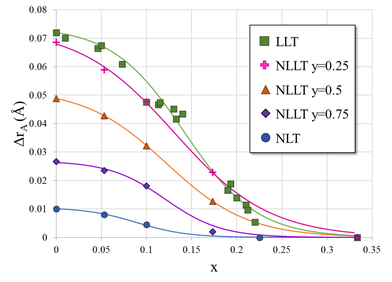

Figure 11: $Na_{(1-3x)/2}La_{(1+x)/2}TiO_3$ (blue), $(Na_yLi_{1-y})_{(1-3x)/4}La_{(1+x)/2}TiO_3$ (y=0.75, purple) (y=0.50, orange) (y=0.25, pink), and $Li_{(1-3x)/2}La_{(1+x)/2}TiO_3$ (green)[2] A-site size adjustment factors as functions of vacancy concentration from experimentally collected data.

5.) $\Delta r_A = \dfrac{a}{1+\exp\left[\dfrac{x+b}{c}\right]}$

6.) $\eta = A + B\ln\left[\dfrac{C}{\Delta r_A} - 1\right]$

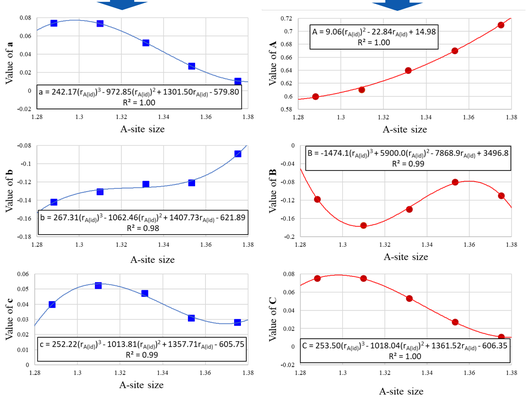

Figure 12: Coefficients of equation (5) (blue squares) as functions of A-site size and coefficients of equation (6) (red circles) as functions of A-site size.

[1] R. Ubic, K. Tolman, K. Talley, B. Joshi, J. Schmidt, E. Faulkner, J. Owens, M. Papac, A. Garland, C. Rumrill, K. Chan, N. Lundy, H. Kungl, Lattice-constant prediction and effect of vacancies in aliovalently doped perovskites, J. Alloys Compd. 644 (2015) 982-995.

[2] K. Tolman, R. Ubic, B. Liu, I. Williamson, K. Bedke, E. Nelson, L. Li, X. Chen, Empirical evidence for A-site order in perovskites, J. Am. Ceram. Soc. 100 (2017) 429-442.

Methods

Stoichiometric powders were milled in deionized water (Figs. 2 and 3), dried in the drying oven (Fig. 4), and calcined at 1100-1200°C (Fig. 5). Phase purity was verified via X-ray diffraction (XRD). Phase-pure powders of $[(Na_yLi_{1-y})_{(1-3x)/2}La_{(1+x)/2}]TiO_3$ (NLLT) and $Ba(Mg_{⅓}Ta_{⅔})O_3$ (BMT) were uniaxially pressed into pellets (Fig. 6). NLLT pellets were sintered on a bed of sacrificial powder on the lid of an inverted crucible at 1300-1400°C (Fig. 7). BMT pellets and some unpressed powders were subjected to each of six heat treatments: 5, 10, 15, 20, 30 or 40 hours at 1500°C. Lattice parameters were obtained from Rietveld refinements performed on the XRD scans of sintered powders using GSAS II.

Figure 2 : Mill pot and milling media

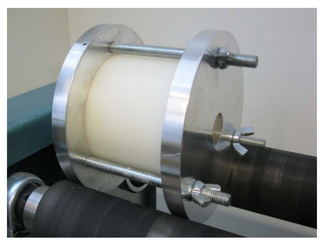

Figure 3 : Rotary mill with mill pot

Figure 4 : Drying pan in drying oven

Figure 5 : Crucible in box furnace chamber

Figure 6 : Uniaxial pellet press

Figure 7 : Inverted crucible with sintered pellets

Conclusion

$(Na_yLi_{1-y})_{(1-3x)/4}La_{(1+x)/2}TiO_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ were synthesized using traditional ceramographic techniques. Empirical models which allow for the prediction of A-site and B-site order parameters using easily obtainable experimental data were made for layered type ordering on the A site and rocksalt type ordering on the B site. The models also allow for the prediction of the A-site and B-site correction parameters (Δr_A and Δr_B) using vacancy concentration and sintering time, respectively. These models could potentially be extended in order to enable the prediction of ordering parameters in other complex perovskite systems from ionic-radii data and experimentally-derived pseudocubic lattice constants alone.

[3] E. Smith, K. Tolman, R. Ubic, An empirical model for B-site cation ordering in $Ba(Mg_{1/3}Ta_{2/3})O_3$, J. Alloys Compd. 735 (2018) 2356-2362.

Acknowledgements

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