Empirical Modeling of Cation Ordering in Perovskite Ceramics

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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. Specifically, models were made for layered type ordering in the \((Na_{y}Li_{1-y})(1:3x)/2La(1+x)/2\)TiO\(_3\) system and rocksalt ordering in Ba(Mg\(_{1/3}\)Ta\(_{2/3}\))O\(_3\).
Empirical Modeling of Cation Ordering in Perovskite Ceramics

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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\text{1-3x}/2La\text{1+x}/2TiO3 (NLLT) system and rocksalt ordering in Ba(Mg\text{3x}/4Ta\text{1-x})O3 (BMT).

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 (Ba\text{1+y}/2La\text{1-x}/2TiO3 (NLLT) and Ba(Mg\text{3x}/4Ta\text{1-x})O3 (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. Lattice parameters were obtained from Rietveld refinements performed on the XRD scans of sintered powders using GSAS II.

Results

B-site ordering data from Ba(Mg\text{3x}/4Ta\text{1-x})O3 (BMT) are presented in figures 8-9. A-site ordering data from (Na\text{1-3x}/2La\text{1+x}/2TiO3 (NLLT) are presented in figures 10-12. 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\cite{1} assumes a disordered structure, so a volume contraction requires a negative \(\Delta A\) term (Eq. 2) which modifies the effective B-site ionic size, \(r\) (Fig. 9). The order parameter, \(\eta\), can now be calculated as a function of either annealing time, \(t\) (Eq. 3), or \(\Delta A\) (Eq. 4).

Conclusions

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References


