

Empirical Modeling of B-site Ordered Triple Perovskites

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Introduction

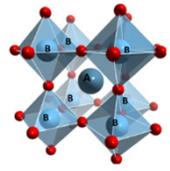


Fig. 1 Illustration of a perovskite structure. A and B cations are labeled, red spheres represent X anions.

A simple perovskite is characterized by its crystal structure and ABX_3 stoichiometry, where A and B are cations and X is an anion¹. The structure is defined by corner-shared anion octahedra, each containing a single B-site cation, with A-site cations in the cuboctahedral spaces between octahedra. Perovskites often have many functional properties such as ferroelectricity and piezoelectricity², which make them promising materials for a wide range of applications such as green-energy, mobile/satellite telephony, computers, automobiles, etc. Given the wide range of potential applications for these materials, it is vital to develop processing-structure-property models which are simple, inexpensive, and easily adaptable to the needs of industry.

With this goal in mind, empirical models have been developed to predict perovskite pseudocubic lattice constants, taking into account the effective size of anions, cations, and even vacancies, using only published ionic radii data. The unit cell is the parallelepiped which defines the translational symmetry of a crystal. It is defined by the basis vectors a , b , c , which are themselves defined by their lengths, a , b , c , and the angles which they make with each other, α , β , γ (the lattice constants). For cubic crystals, $a=b=c$ and $\alpha=\beta=\gamma=90^\circ$, so a single lattice constant, a , is sufficient. For trigonal perovskites, where $a=b \neq c$, a pseudocubic lattice constant, a_{pc} , can be defined as:

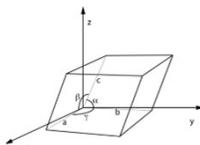


Fig. 2 A simplified unit cell with side lengths a , b , and c , and angles α , β , and γ .

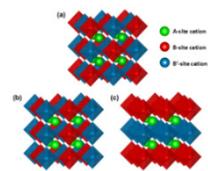


Fig. 3 Examples of types of B-site ordering in perovskites

When multiple cations are introduced at the B site of a perovskite, they can either be **ordered** or **disordered** (distributed randomly). As per Smith et al.³, a perovskite with a high degree of B-site order exhibited **volume shrinkage**, observed as a decrease in the lattice constant. The **ordering parameter**, η , describes the extent of ordering in the structure, with 0 being completely disordered and 1 being completely ordered. An empirical model was developed for B-site ordering in $BaMg_{1/3}Ta_{2/3}O_3$ (BMT). It was found that longer annealing times led to predictably greater ordering and volume shrinking. Due to the similarities between the two compositions, the BMT paper's³ methodology was followed closely, with the goal of achieving higher ordering with BSMT.

The objective of this project is to produce highly ordered **Barium Strontium Magnesium Tantalate** (BSMT) samples and use the collected experimental data to assist in creating a predictive model for the a_{pc} of 1:2 ordered perovskites. Towards this end, three 1:2 ordering triple perovskites in the form of $(Ba_{1-x}Sr_x)(Mg_{1/3}Ta_{2/3})O_3$ were synthesized and analyzed for a_{pc} and η .

Abbreviation	Chemical Formula
$x = 0.25$	$(Ba_{0.75}Sr_{0.25})(Mg_{1/3}Ta_{2/3})O_3$
$x = 0.5$	$(Ba_{0.5}Sr_{0.5})(Mg_{1/3}Ta_{2/3})O_3$
$x = 0.75$	$(Ba_{0.25}Sr_{0.75})(Mg_{1/3}Ta_{2/3})O_3$

Table 1. Perovskite compositions created in this project

Methodology

Step 1: Combine stoichiometric amounts of $BaCO_3$, $SrCO_3$, $4MgCO_3 \cdot Mg(OH)_2 \cdot 4(H_2O)$, and Ta_2O_5 in nylon pot partly filled with YSZ milling media.



Step 2: Add 1 wt% Dispx A40 (deflocculant) and fill to ~80% full with deionized water. Ball mill for 4 hours.



Step 3: Dry mixture at 98°C in drying oven for 12 hours or until completely dry. Crush dried mixture with a mortar and pestle, then sieve powder to <250 μm .



Step 4: Calcine sample at 1200°C for 12 hours using a heating/cooling rate of 3°C/min.



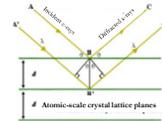
Step 5: Ball mill calcined sample with deionized water for 24 hours, adding 2 wt% PEG 10,000 for last 3 minutes of milling.



Step 6: Repeat Step 3 then anneal powder at 1500°C for 30 hours with a heating/cooling rate of 4°C/min.



Step 7: Analyze powders produced in Step 4 (calcined) and pellets produced in Step 6 (annealed) using X-ray diffraction (XRD) to confirm phase purity.



Step 8: Use Bragg's Law to calculate the lattice constant from the peak angles found in XRD. Compare observed vs theoretical lattice constant to find the ordering parameter.

$$\text{Bragg's Law: } n\lambda = 2d\sin(\theta)$$

Methodology adapted from Smith et al. 2018³.

Results

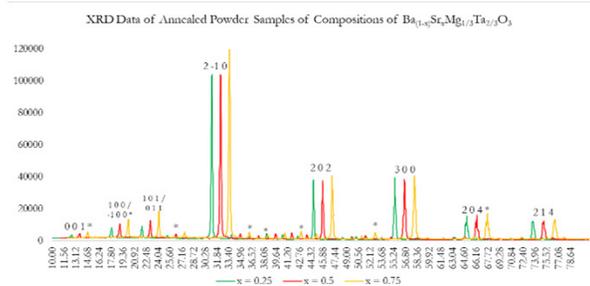


Fig. 4 Graph of x-ray diffraction data from compositions of BSMT. All samples were annealed at 1500°C for 30 hours. Miller indices for each peak are shown above, and asterisks indicate ordering peaks. The $x = 0.5$ dataset has been offset +1° and the $x = 0.75$ dataset has been offset +2° for visual clarity.

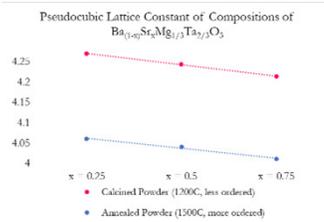


Fig. 5 Graph of a_{pc} of calcined and annealed BSMT powder samples of varying compositions

BSMT Compositions	$\Delta\eta^*$
$(Ba_{0.75}Sr_{0.25})(Mg_{1/3}Ta_{2/3})O_3$	-0.04107
$(Ba_{0.5}Sr_{0.5})(Mg_{1/3}Ta_{2/3})O_3$	-0.03766
$(Ba_{0.25}Sr_{0.75})(Mg_{1/3}Ta_{2/3})O_3$	-0.03579

Table 2. Calculated $\Delta\eta$ values of $x = 0.25$, $x = 0.50$, and $x = 0.75$ BSMT compositions.

* $\Delta\eta$ is not accurate, but displays a close approximation

Ordering parameter for all three compositions is 94% according to Rietveld refinements

Discussion

XRD graphs

- The x-ray diffraction data for all six samples showed strong evidence for successful synthesis of the desired BSMT phase. Fig. 4 shows how the measured peaks line up with the database peaks for SMT ($x=1$) and BMT ($x=0$), but are slightly closer to the SMT peaks because this composition contains 75% Sr.

Lattice Constants

- Sr has a smaller atomic radius than Ba, so higher Sr compositions should have a smaller a_{pc} . The largest a_{pc} was indeed observed for the $x=0.25$ composition and the smallest lattice constant for the $x=0.75$ composition. Therefore, a_{pc} decreases monotonically with increasing x , as expected.
- These results suggest that volume shrinkage occurred during the longer, higher temperature annealing period because for all three compositions, the annealed powder has a smaller a_{pc} than the calcined powder.
- Mathematically, $\Delta\eta$ being negative also supports volume shrinkage³ with respect to the disordered form.

Ordering

- Decreasing lattice constant suggests volume shrinkage and increased ordering after annealing.
- After completing Rietveld refinements, the ordering parameter for all three BSMT compositions is 94%, thus implying higher ordering, η

Further Studies

- Use this data in conjunction with data from Inorganic Crystal Structure Database (ICSD) to create a predictive pseudocubic lattice constant and ordering mathematical model for 1:2 ordered triple perovskites.
- Define a more accurate $\Delta\eta$ in order to predict ordering.

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