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Empirical Modeling of B-site Ordered Perovskites

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Abstract

Complex perovskites of the form $AB_{0.5}B'_{0.5}X_3$, where A, B, and B' are cations and X is an anion, abound in technological applications. In many cases B and B' cations chemically order on crystallographically unique sites, influencing properties and resulting in a volume shrinkage. In this work, various compounds including $(Ba_{0.5}Sr_{0.5})(Mg_{0.5}W_{0.5})O_3$ and $(Sr_{0.5}Ca_{0.5})(Mg_{0.5}W_{0.5})O_3$ as well as several compositions in the $[(Ca, Sr, Ba)_{1-3x}La_{2x}](Mg_{0.5}W_{0.5})O_3$ series were made via conventional techniques. In particular, the $[(Ca, Sr, Ba)_{1-3x}La_{2x}](Mg_{0.5}W_{0.5})O_3$ system allows the effect of B-site ordering on effective ionic sizes and cell volume to be studied as a function of A-site size as the host crystal changes from cubic (A=Ba) to tetragonal (A=Sr) to monoclinic (A=Ca). Data mining was also employed to include the host of other reported ordered perovskites in a model for the prediction of the effective change in B-site size, Δr_B , upon ordering. Such a model would allow the prediction of structures with little or no experimental data, thus eliminating much of the trial and error and drastically reducing material-development time and costs. The goal of this project is to establish a generic numerical model for the effective ionic radii and lattice constants for complex perovskites containing B-site ordering.

Method

Solid-state mixed-oxide methods were used to create batches of double perovskite oxides. Specifically, $(Sr_{0.5}Ca_{0.5})(Mg_{0.5}W_{0.5})O_3$, $(Ba_{0.5}Sr_{0.5})(Mg_{0.5}W_{0.5})O_3$, and $[(Ca, Sr, Ba)_{1-3x}La_{2x}](Mg_{0.5}W_{0.5})O_3$ ($x=0.1, 0.15, 0.2, 0.25$) compositions were made.

Raw powders were milled in deionized water for 4-6 hours (Fig. 3). Slurries were then dried, crushed, and sieved before being calcined for 24-30 hours at 850-1200°C (Figs. 4-6). X-ray diffraction (XRD, Miniflex 600, Rigaku) data were then obtained to verify phase purity. Data refinement using GSAS II software^[4] was used to obtain lattice parameters. These data, along with data from literature, were used to create an empirical model. A B-site cation radius correction term, Δr_B , was added to the ideal B-site radii in order to minimize errors in calculated a_{pc} values. These correction values were graphed as functions of a_{pc} and t' to derive the empirical model sought.

Figure 3: Mill pot on mill



Figure 4: Batches in drying oven



Figure 5: Crushing and sifting powder

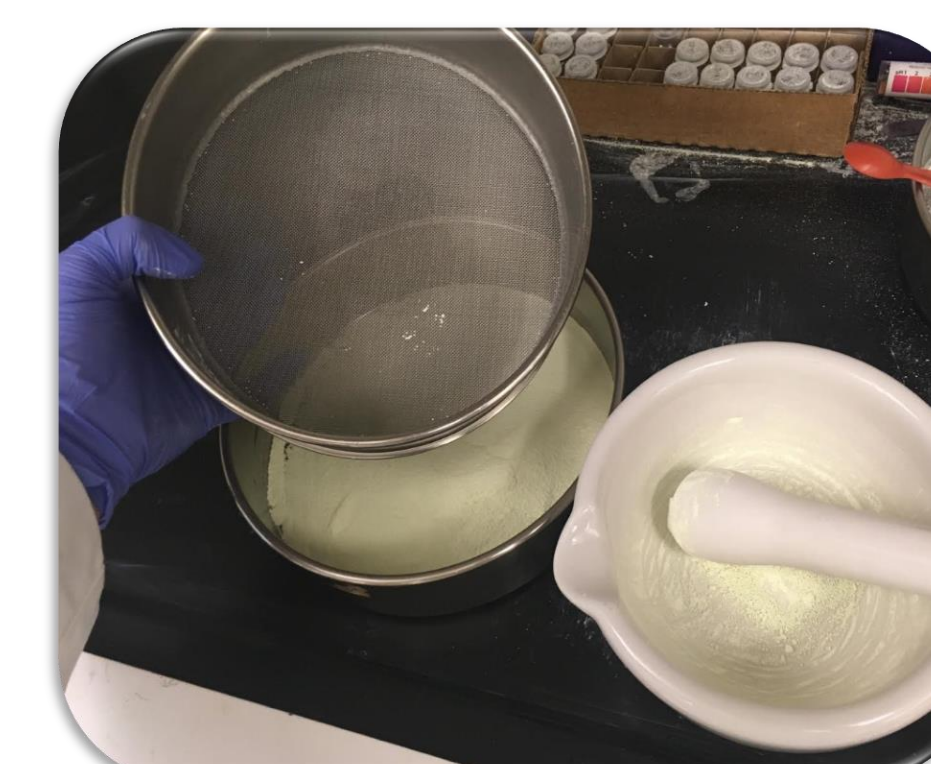


Figure 6: Crucible in furnace during calcining process

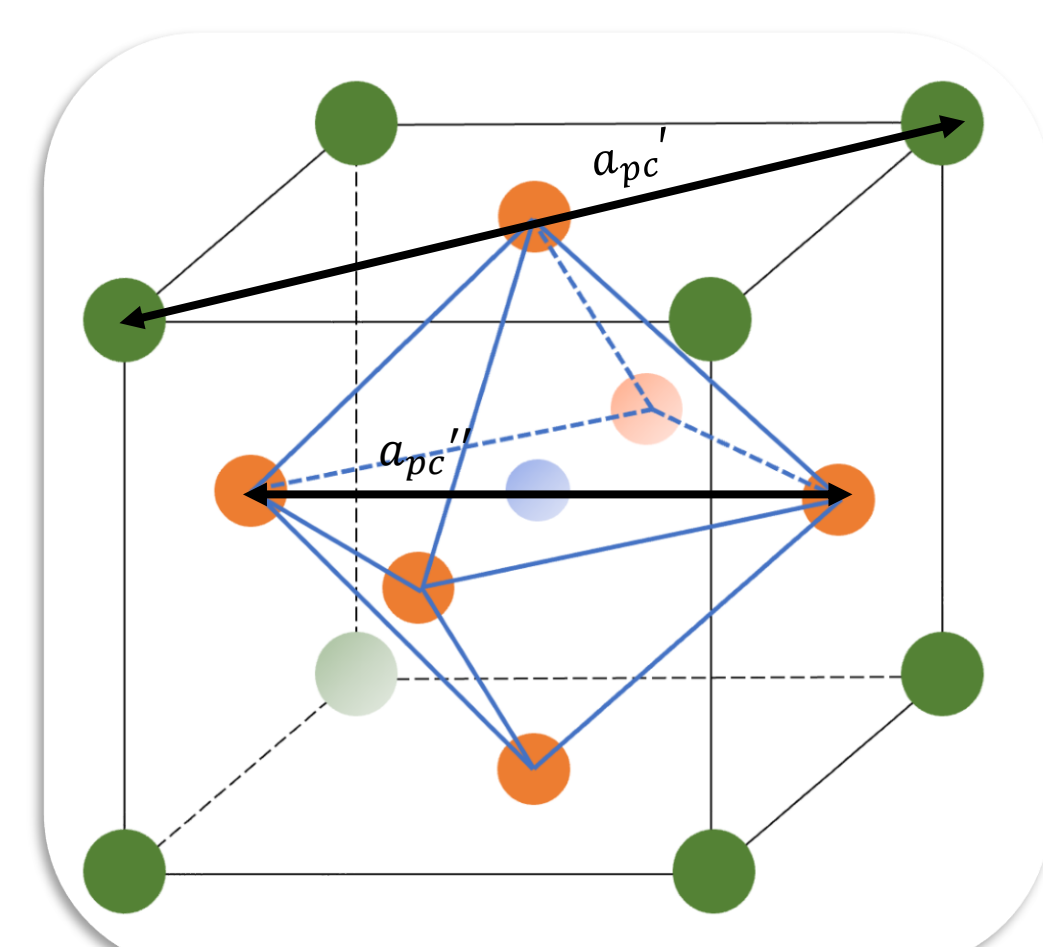


Figure 1: Archetypical perovskite unit cell

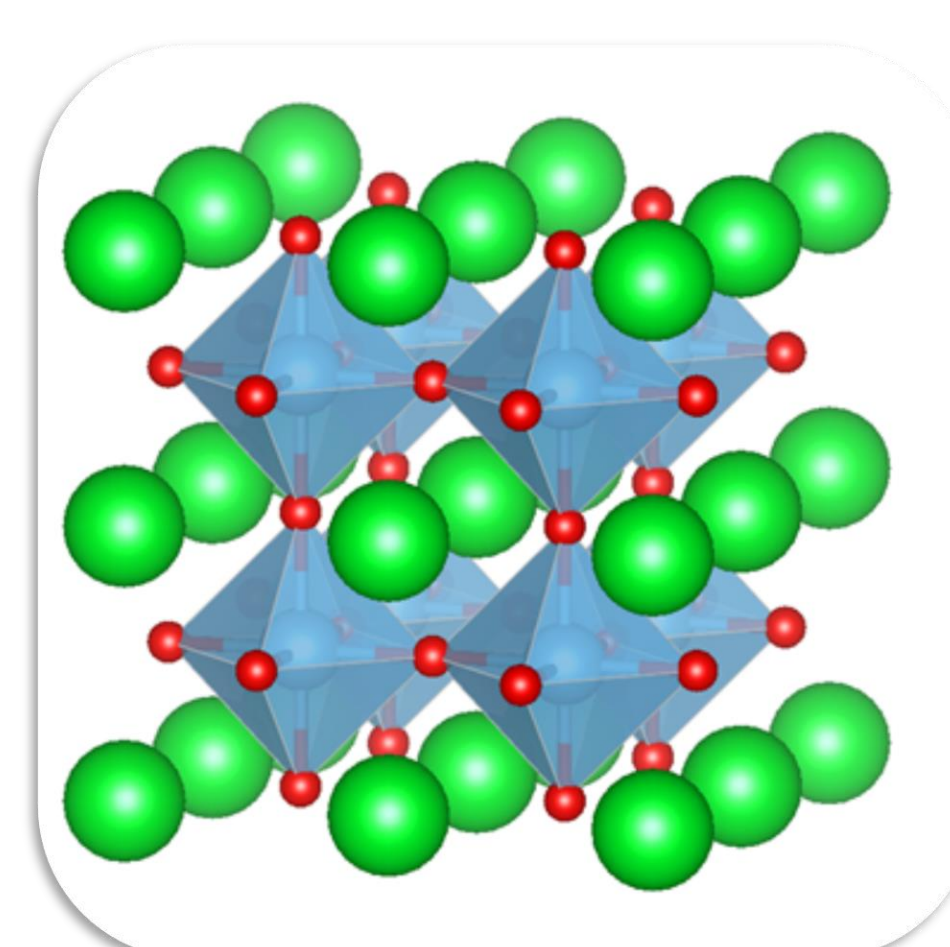


Figure 2: Eight perovskite unit cells showing corner-shared octahedra

Introduction

The term perovskite refers to any compound that shares the structural elements depicted in Figs. 1-2. Ubic *et al.*^[1] created a model to predict pseudocubic lattice constants in terms of A-X and B-X bond lengths, a'_{pc} and a''_{pc} , respectively, which accounted for point defects within the structure; where r_B , r_A , and r_X are the effective radii size for each A, B, and X-site respectively, and $r_{X(id)}$ is the ideal radii size of the X-site. (Eqns. 1-3) The tolerance factor, t' , was also redefined in terms of the conventional Goldschmidt tolerance factor, t , and the ideal ionic radius of the A-site containing no vacancies ($r_{A(id)0}$) (Eqn. 5). Later, Tolman *et al.*^[2] proved that layered A-site ordering causes a volume expansion while rock-salt B-site ordering causes a volume shrinkage. The former effect has since been quantified by Smith *et al.*^[3] The goal of this project is to develop a numerical model to quantify the effect of B-site chemical ordering.

- 1) $a_{pc} = 0.7209203(t' + 1.760998)(r_B + r_{X(id)}) + 0.011730139$
- 2) $a'_{pc} = \sqrt{2}(r_A + r_X')$
- 3) $a''_{pc} = 2(r_B + r_X')$
- 4) $r_X' = r_{X(id)}(0.42983 + 0.56696t')$
- 5) $t' = A + Bt + Ct^2$

$$A = -50.978 + 84.274r_{A(id)0} - 32.411r_{A(id)0}^2$$

$$B = 130.35 - 205.44r_{A(id)0} + 77.539r_{A(id)0}^2$$

$$C = -81.294 + 124.73r_{A(id)0} - 46.185r_{A(id)0}^2$$

Results

X-ray diffraction data show phase pure powders of $(Ca_{1-3x}La_{2x})(Mg_{0.5}W_{0.5})O_3$ $x=0.15, 0.2$ and $(Sr_{0.5}Ca_{0.5})(Mg_{0.5}W_{0.5})O_3$ batches. Refinements of these XRD patterns were produced and used to obtain lattice parameters of the structure. This information was added to data from literature and graphed (Fig. 7-9).

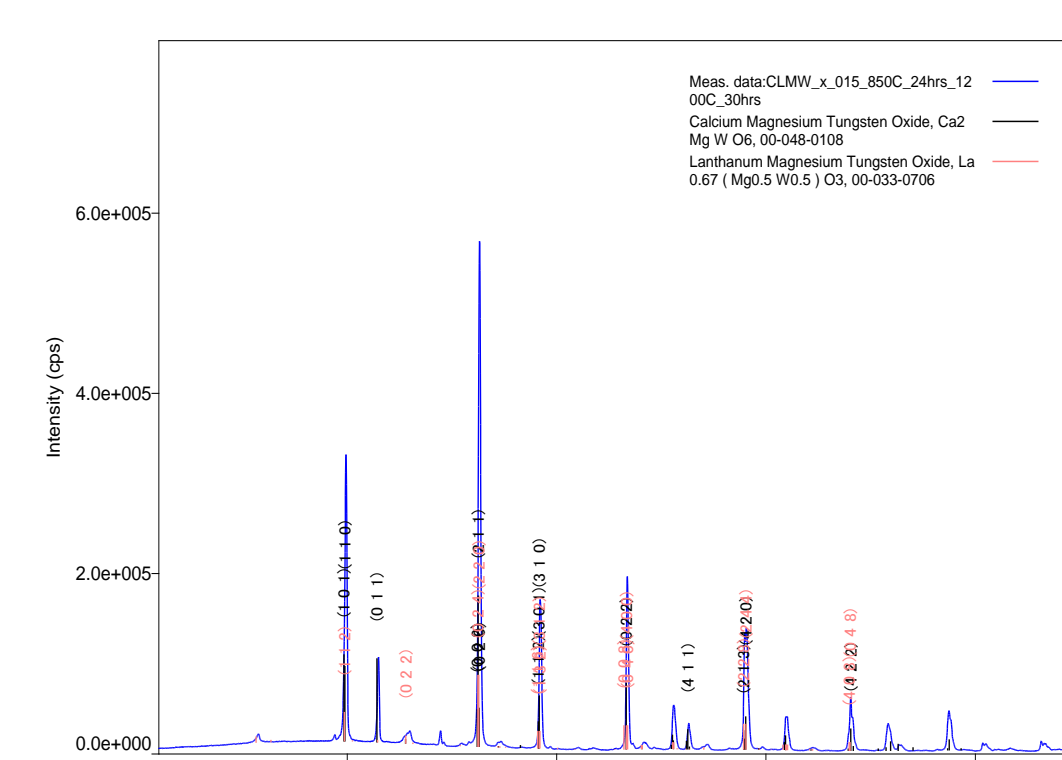


Figure 7: $(Ca_{1-3x}La_{2x})(Mg_{0.5}W_{0.5})O_3$ $x=0.15$ XRD result

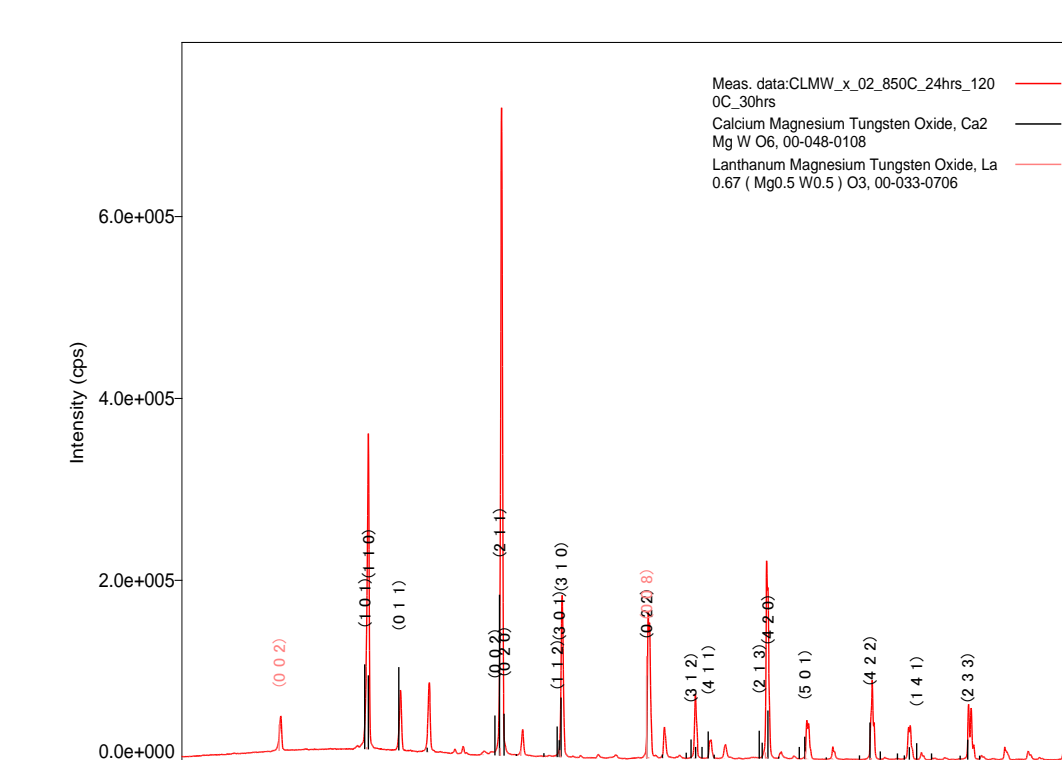


Figure 8: $(Ca_{1-3x}La_{2x})(Mg_{0.5}W_{0.5})O_3$ $x=0.2$ XRD result

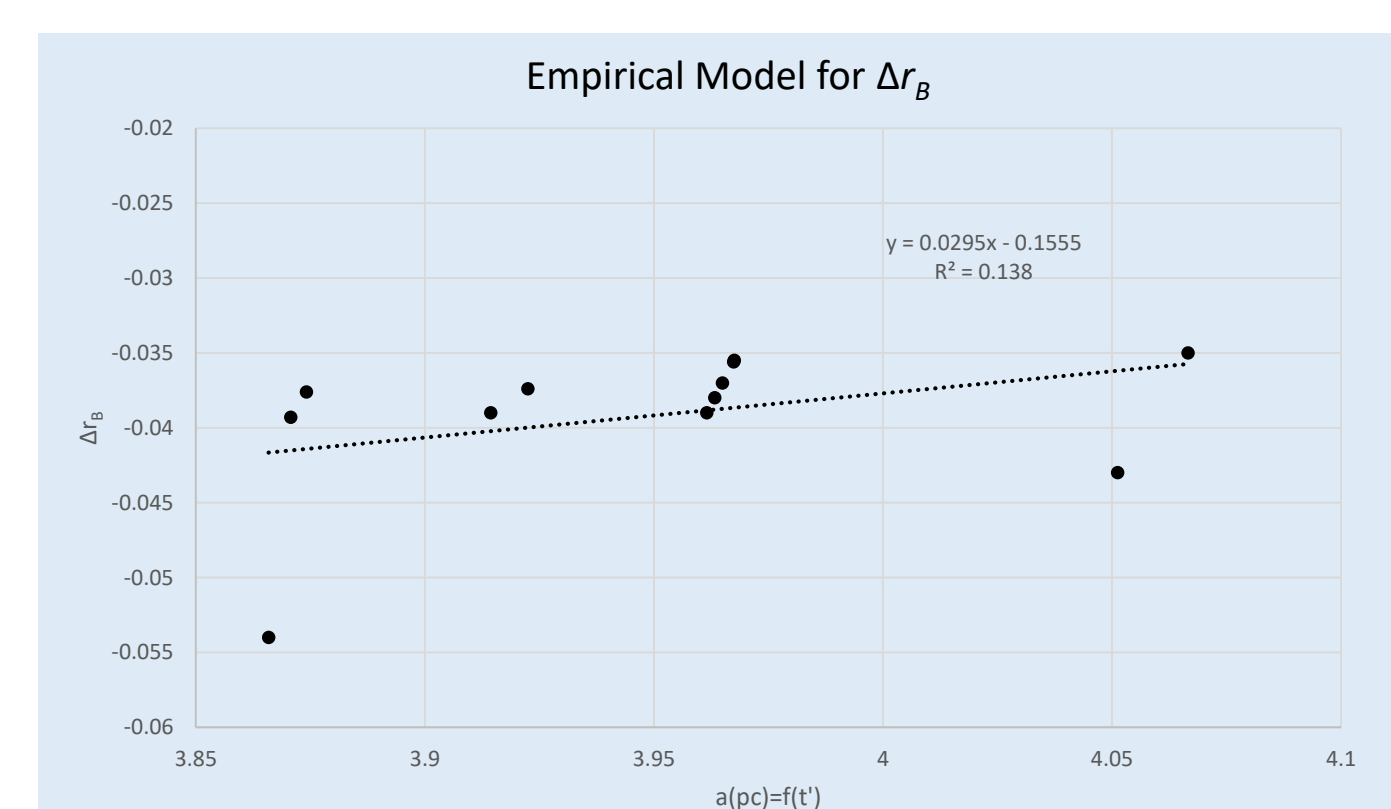


Figure 9: Attempt at finding a trend within the data, simultaneously minimizing errors in a_{pc} , a'_{pc} and a''_{pc} , where the absolute average relative error was no more than 0.33%.

Further Studies

It would be useful to re-calcine the $(Ba_{0.5}Sr_{0.5})(Mg_{0.5}W_{0.5})O_3$ and $[(Sr, Ba)_{1-3x}La_{2x}](Mg_{0.5}W_{0.5})O_3$ batches in order to improve phase purity and thereby obtain more data points for the model.

Trends were not found for B-site ordering within the time of this research experience. Upon further research, perhaps results similar to those of Smith *et al.*^[5] (Fig. 10) could be produced; however, other factors may play a role in volume changes upon ordering and could possibly be used to improve the model.

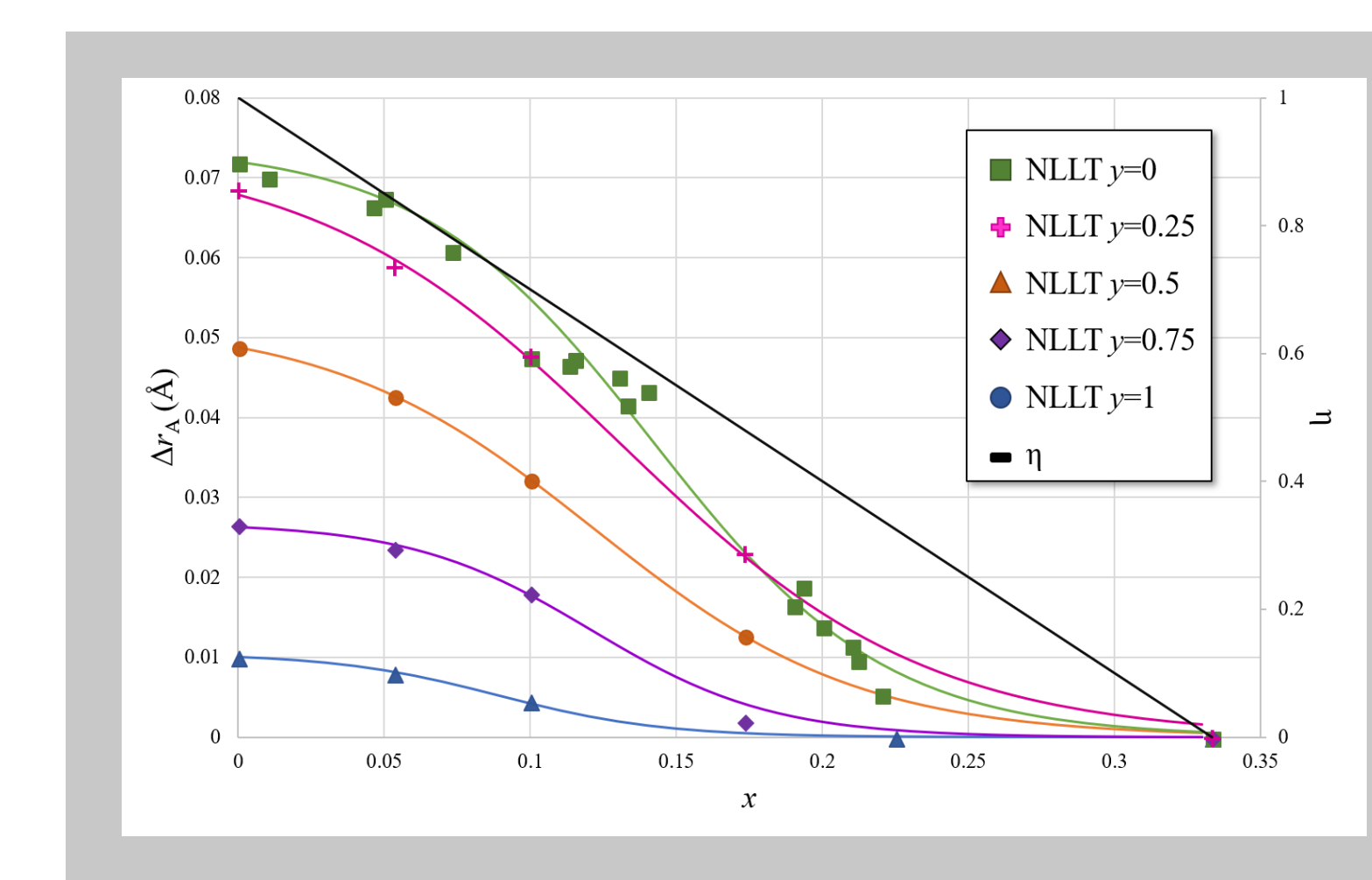


Figure 10: A-site size adjustment factors as functions of composition from experimentally collected data for $(Na_xLi_{1-x})_{1-3x}/2La_{(1+x)/2}TiO_3$ and A-site order parameter, η , as a function of composition.

Acknowledgements

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[1] Ubic, R., et al. "Lattice-Constant Prediction and Effect of Vacancies in Aliovalently Doped Perovskites." *Journal of Alloys and Compounds*, vol. 644, 16 May 2015, pp. 982-995. doi:10.1111/jace.14547.
 [2] Tolman K, Ubic R, Liu B, et al. "Empirical Evidence for A-site Order in Perovskites." *Journal of the American Ceramic Society*, vol. 100, 2017, pp. 429-442. doi:10.1111/jace.14547.
 [3] Smith E, Tolman K, Ubic R. "An Empirical Model for B-site Cation Ordering in $Ba(Mg_xTa_{1-x})O_3$." *Journal of Alloys and Compounds*, vol. 735, 25 February 2018, pp. 2356-2362. https://doi.org/10.1016/j.jallcom.2017.11.333.
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 [5] Smith E, Ubic R. "Empirical Models for Layered A-site Ordering in Perovskite Titanates." 2018. Unpublished.

