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Expanding Empirical Models of Perovskites

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Abstract

Perovskites are ubiquitous in modern devices because their wide compositional range and structural variability gives rise to useful properties like piezoelectricity, pyroelectricity, ferroelectricity, superconductivity, colossal magnetoresistance, proton conduction, catalysis, and spin-dependent transport. While a few theoretical models exist for the structure of some perovskite structures, few are suited to the doped ceramics used in commercial devices. An entirely new empirical modelling technique was recently developed, and this work aims to expand the validity limits of that model. Specifically, the goal was to extend the model to accommodate perovskites containing cuboctahedrally-coordinated cations which are smaller than 1.34 Å (Ca²⁺). Toward that end, some of the Ca²⁺ in Ca_{1-3x}La_{2x}TiO₃ was replaced with Mg²⁺ (~1.2 Å); however, it was found that [(Ca_{1-y}Mg_y)_{1-3x}La_{2x}]TiO₃ solid solutions did not form, rather, mixtures of pure Ca_{1-3x}La_{2x}TiO₃ and MgTiO₃ resulted.

Introduction

Understanding the behavior of perovskites extends back to 1926 when Goldschmidt [1] proposed a tolerance factor (*t*) to describe the stability of the perovskite structure. This model is limited in that it makes no account for effects of chemical environment on ionic size. In 2015, Ubic [1] derived an improved tolerance factor (*t*₁), and this model proves more accurate in many cases. [1] An extreme example is in the system MgSiO₃ where uncertainty in the size of Mg²⁺ yields a *t*~1.0436, suggesting an untitled structure. Ubic's model yields *t*₁=0.9546 which agrees with the tilted *Pbnm* structure reported experimentally. [2]

$$t_* = \frac{r_{A(id)} + r_{X(id)}}{\sqrt{2}(r_B + r_{X(id)})} \quad t_1 = \frac{a_{pc} - 0.011730139}{0.7209203(r_B + r_{X(id)})} - 1.760998$$

Equations 1 and 2. Goldschmidt's (left) and Ubic's (right) equations for tolerance factor, where *r*_{A(id)}, *r*_B, and *r*_{X(id)} are the ionic radii of A, B, and X ions, respectively, while *a*_{pc} is the lattice constant of the pseudo-cubic cell. [1]

Although *t*₁ is more accurate than *t* at characterizing perovskites, it still has limitations in that it requires knowledge of the lattice parameters. This limitation can be overcome by plotting *t*₁ versus *t* for a range of compositions in the A_{1-3x}La_{2x}TiO₃ system (Fig. 1) and then taking a polynomial regression for their relationship for each family of compositions. [1]

The data for the compositions in figure 1 come from literature, except for the Sr_{1-3x}La_{2x}TiO₃ family which Ubic's group synthesized themselves.

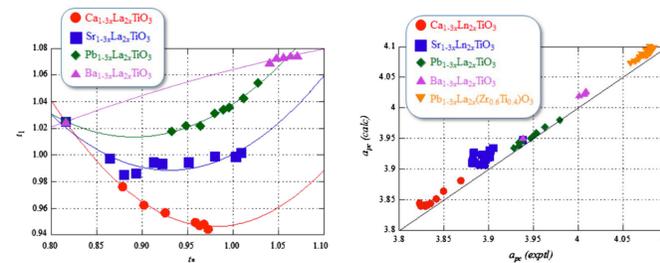


Figure 1. (left) Relationship between *t*₁ in A_{1-3x}La_{2x}TiO₃ (A = Ca, Sr, Pb, Ba). (right) Comparison of calculated and experimental *a*_{pc} values using Ubic's equations for *t*₁.

The resulting equations allow *t*₁ to be calculated from *r*_{A(id)}, *r*_B, and *r*_{X(id)}.

$$t_1 = A + Bt_* + Ct_*^2$$

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

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

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

Equation 3. Polynomial regression for calculating *t*₁ as a function of *t*. [1]

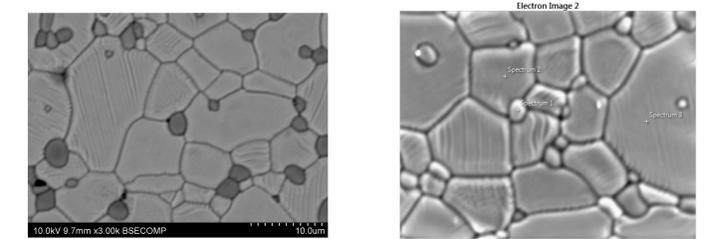
While this model is useful, it only applies to perovskites whose A-site radii are within the range 1.34 Å (Ca²⁺) and 1.61 Å (Ba²⁺). The next logical step in expanding the model to accommodate A-sites with small radii would be to explore MgTiO₃; however, this compound forms in the ilmenite, not perovskite, structure. [3] For this reason, Mg²⁺ was used as a dopant in Ca_{1-3x}La_{2x}TiO₃ in order to reduce that the size of the A-site while maintaining a perovskite structure.

Method

Compositions in the system (Mg_{0.1}Ca_{0.9})_{1-3x}La_{2x}TiO₃ were processed via the solid-state mixed-oxide method. The compositions were calcined twice for 3 hours at 1150° C and ball-milled before each calcination. Phase assemblage was verified via x-ray diffraction (XRD) and lattice constants were determined via Rietveld refinements. To confirm the compositions of the given phases, pellets were sintered at 1350° C, polished, and thermally etched for back scatter electron imaging via scanning electron microscopy (Hitachi S-3400N). Energy dispersive x-ray spectroscopy (EDS, Oxford Instruments Engery+ resolution < 136eV) confirmed the composition of the phases observed.

Results

No compositions in the (Mg_{0.1}Ca_{0.9})_{1-3x}La_{2x}TiO₃ solid solution were successfully made as Mg²⁺ does not readily substitute for Ca²⁺ in CaTiO₃. This result was confirmed via both back-scattered electron (BSE) images and EDS (Fig. 2). The BSE images show two distinct phases, the lighter grains corresponding to Ca_{1-3x}La_{2x}TiO₃ and the darker ones to MgTiO₃. Apparently, the goal of this project could not be achieved with the experimental approach used.



x = 0.1	Mg (at%)	Ca (at%)	Ti (at%)
Spectrum 1	13.67	0.51	14.01
Spectrum 2	0.12	15.19	16.18
Spectrum 3	0	15.55	16.65

Figure 2. (above) BSE image (left) in which bright grains are Ca_{1-3x}La_{2x}TiO₃ and dark grains are MgTiO₃. A secondary-electron image (right) is also shown. (below) EDS results showing the atomic percent of Mg and Ca in each of the perovskite and ilmenite phases.

Conclusion and Future Work

This method of forming a Mg²⁺ doped Ca_{1-3x}La_{2x}TiO₃ perovskite proved to not be possible. Instead, a mixture of MgTiO₃ and MgTi₂O₅ resulted with not apparent trend of one species propagating over the other.

Although this approach to creating a perovskite with a small A-site proved to be unsuccessful, there does exist another option in the MgSiO₃ system. Normally MgSiO₃ forms with the pyroxene structure; however, Dobson and Jacobsen [2] have developed a flux-growth method for growing large single crystals of perovskite MgSiO₃. This approach is the next logical step in achieving this project's goals.

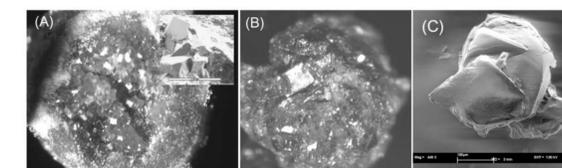


Figure 3. Single crystals of perovskite MgSiO₃ from the work of Dobson and Jacobsen. [2]

[1] R. Ubic *et al.*, "Lattice-constant prediction and effect of vacancies in aliovalently doped perovskites," *Journal of alloys and compounds*, vol. 644, pp. 982-995, 2015.

[2] D. P. Dobson and S. D. Jacobsen, "The flux growth of magnesium silicate perovskite single crystals," *American Mineralogist*, vol. 89, no. 5-6, pp. 807-811, 2004.

[3] R. Ubic, K. Tolman, K. Chan, N. Lundy, S. Letourneau, and W. Kriven, "Effective size of vacancies in aliovalently doped SrTiO₃ perovskites," *Journal of Alloys and Compounds*, vol. 575, pp. 239-245, 2013.

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