Empirical Modeling of Trigonal Distortions in Perovskites

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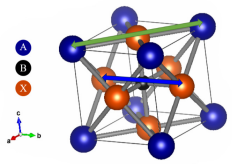
Abstract

Data-driven models explaining structure-property relationships in engineering systems can significantly reduce development time. Additionally, these models help to mitigate material costs by eliminating unnecessary use of raw materials in nonviable material systems. There are a few such models for perovskite systems, but none for those containing trigonal distortions or oxygen vacancies. In this study, structural data for five trigonally distorted perovskite systems were mined from literature, and a correlative relationship between the trigonality and the tolerance factor was derived. The general equation predicts the potential trigonality of a given perovskite system at room temperature and pressure using only ionic radii data. As intrinsic polarization is directly related to these distortions, it may be possible to predict that as well.

Introduction

- Perovskites are useful in a range of functional applications.
- Properties inherent to perovskites, such as piezoelectricity, are structure-dependent



- Predicting structure for various perovskites streamlines research and saves on costs

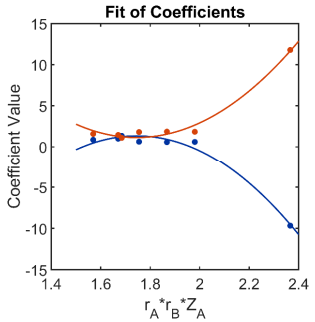
Method

- Structural data mined from existing literature
- Tolerance factor, A-site size, oxygen size, and the degree of trigonality (*c*/*a* ratio) were calculated
- Trigonality was compared to values calculated from structural data to develop an empirical model

Results/Conclusion

There is a correlative relationship between trigonality and the tolerance factor, A-site size, and oxygen size in perovskites. Figure below shows fit of A (blue) and B (orange) coefficients of the linear equation used to fit individual series.

$$c/a = A \cdot t' + B$$



Similar work will be carried out in perovskite systems with stoichiometric oxygen vacancies to further expand the understanding of perovskite structure-property relationships.

Structural distortions of **perovskite** ceramics can be **accurately predicted** using only published **ionic-radius data.**

Further Background

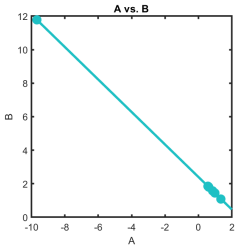
New models have recently been developed for pseudocubic lattice constant, A-site ordering, and B-site ordering. This work helps to develop a more complete picture of perovskites by addressing non-cubic trigonal distortions.

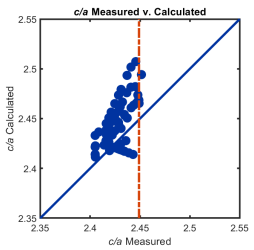
Why does predicting structure matter? Example - Ferroelectricity

- Dependent on charge displacement within a volume (non-cubic distortion), creating a dipole
- Understanding structural changes leads to understanding of ferroelectric properties and better engineering control

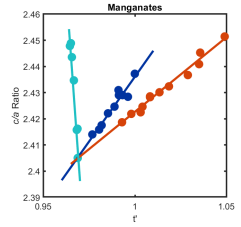
Examples and Additional Plots

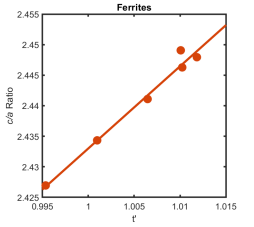
- Below: Correlation between A and B coefficients (left). Coefficients used to fit series are related and the model can therefore be solved by determining only one. Calculated *c/a* vs. measured *c/a* (right). Model is shown to be a fairly good predictor
- Coefficients fit with following equations:
  $A = -28.13 \cdot x^2 + 98.18 \cdot x - 84.34$
  $B = 27.23 \cdot x^2 - 95 \cdot x + 83.99$

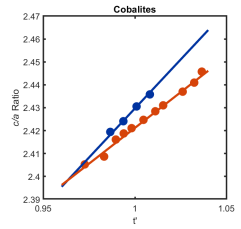


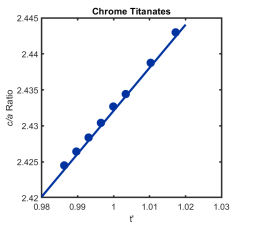


- Clockwise from top left: manganate series ($LaSrMnO_3$, $LaCaMnO_3$, $LaBaMnO_3$), ferrite series ($LaSrFeO_3$), chrome titanates ($BaLaTiCrO_3$), and cobalites ($LaSrCoO_3$, $BaSrCoO_3$)









Sources and Acknowledgements

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