PEROVSKITE NITRIDES: A NEW PLAYGROUND FOR FUNCTIONAL MATERIALS

Geoff Brennecka, Colorado School of Mines
geoff.brennecka@mines.edu
Kevin Talley, Colorado School of Mines
Rachel Sherbondy, Colorado School of Mines
Andriy Zakutayev, National Renewable Energy Laboratory

Key Words: Perovskite, Nitride, Piezoelectric, Semiconductor, Ferroelectric

The perovskite crystal is a favorite playground for electroceramists across a wide variety of applications, and recent developments on hybrid metallorganic perovskite photovoltaics has renewed interest in expanding the chemical space of this flexible and multifunctional crystal structure. A survey of experimentally confirmed simple perovskite compounds (ABX_3) finds no reports of pure X=N anion chemistries. One challenge of forming nitride perovskite materials is the high valence cations needed to satisfy the high valency of nitrogen; another is limiting oxygen impurities. Computational predictions of energetically favorable nitride perovskites have been reported[1] and DFT+LDA methods[2] suggest that the lowest energy state of $LaWN_3$ is a non-centrosymmetric R3c type distorted perovskite structure with a spontaneous polarization of approximately 60μC/cm^2 along the <111> polar axis. A relatively low energy barrier predicted for polarization reversal raises the possibility of ferroelectricity as well. Developing a ferroelectric nitride would greatly simplify integration of a number of functional (e.g., ferroelectric, piezoelectric, and more) properties directly with nitride semiconductors for a variety of integrated sensing and energy conversion applications. Here we report the experimental confirmation of oxygen-free $LaWN_3$ as a perovskite (Fig. 1) using multiple fabrication approaches. Calculations show 5 different symmetries with very similar lattice energies (3 polar and 2 non-polar); refinements of x-ray and electron diffraction in conjunction with property measurements document the complexity of the $LaWN_3$ system in addition to other closely-related perovskite nitrides.

[1] R. Sarmiento-Pérez et. al., *Chemistry of Materials*, 27, 5957 (2015)
[2] Y. Fang et. al., *Physical Review B,*95, 014111 (2017)

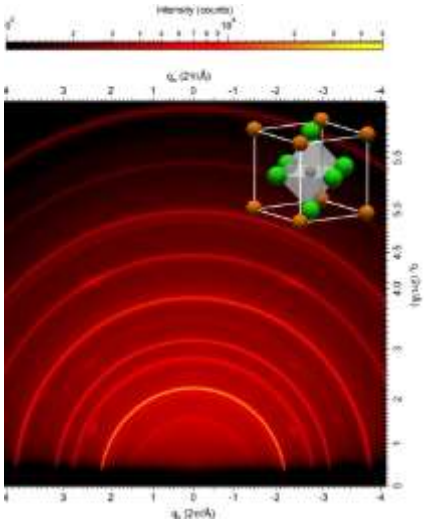

Figure 1 – Diffraction pattern confirming fabrication of the first-reported nitride piezoelectric, $LaWN_3$.