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ABSTRACT:

On the Origin of Non-Classical Electrostriction in Ion Conductors

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Electrostriction is a second order electromechanical response observable in all solid dielectrics. According to the scaling law presented more than two decades ago by Prof. R. Newnham (Penn State), the electrostriction polarization coefficient for a wide range of classical electrostrictors scales with the ratio of the elastic compliance to the dielectric constant.

In 2012, Gd-doped ceria, one of the most studied oxygen ion conductors, was reported to exhibit an unusually large electrostriction. This first report was followed by reports on non-classical electrostriction (NCES) in other aliovalent-doped ceria, on (Nb,Y)-stabilized cubic Bi₂O₃ and acceptor-doped, hydrated barium zirconate, suggesting that strong electrostriction may be an inherent property of superionics. At room temperature, these ceramics exhibit a longitudinal electrostriction strain coefficient $|M_{33}| > 10^{-17} \text{ m}^2/\text{V}^2$. However, with elastic modulus $> 80 \text{ GPa}$ and dielectric constant < 100 , the experimental Q-coefficients of these materials are at least 100 times larger than values predicted by the classical scaling law. Of the three ceramics, aliovalent-doped ceria is the most studied. Below 1 Hz, $|M_{33}|$ for 10 mol% Sm- or Gd-doped ceria reaches $10^{-16} \text{ m}^2/\text{V}^2$ relaxing to $< 10^{-18} \text{ m}^2/\text{V}^2$ above 100 Hz. Aliovalent lanthanide dopants with smaller ionic radii than that of Gd, such as Lu or Yb, raise $|M_{33}|$ at 100 Hz to $\approx 10^{-17} \text{ m}^2/\text{V}^2$.

Acceptor-doped BaZr_{1-x}X_xO_{3-x/2+δ}H_{2δ} proton-conducting ceramics, where X = Ga, Sc, In, Y or Eu, and $0.05 \leq x \leq 0.2$, exhibit non-classical electrostrictive strain for all dopants in both the dry and hydrated states: $|M_{33}| = (1-7) \cdot 10^{-16} \text{ m}^2/\text{V}^2$ below, and $\approx 10^{-18} - 10^{-17} \text{ m}^2/\text{V}^2$ above, the Debye-type relaxation frequency. Hydration does not significantly affect M_{33} , but raises the relaxation frequency by a factor of 10 to 100, indicating that proton-based elastic dipoles can respond more quickly than those based on oxygen vacancies.

According to our current understanding, NCES emerges from electric field-induced rearrangement of highly polarizable elastic dipoles induced by point defects: oxygen vacancies or proton interstitials. In this model, elastic and dielectric properties are largely defined by the host lattice, while electrostrictive strain is controlled by the strength of the elastic dipoles. We suggest that non-classical electrostriction may be a common feature for crystalline dielectrics containing mobile point defects.