Giant Electrostriction in Ionic Conductors

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Abstract

We have recently reported that three well-studied ionic conductors, Gd-doped ceria, (Nb, Y)-stabilized cubic bismuth oxide and Y-doped hydrated barium zirconate, exhibit large electrostriction, a quadratic induction of strain by an electric field. At room temperature, all three materials exhibit a strain electrostriction coefficient (M11) exceeding 10^{-17} \text{m}^2/\text{V}^2 and can generate stress of tens of MPa without saturation. Classical theory of electrostriction, introduced two decades ago by Prof. R. Newnham (Penn State), predicts that the electrostriction polarization coefficient (Q) scales with the ratio of elastic compliance to dielectric constant. This theory successfully describes most classes of materials from polymers, generating large strain and small stress, to relaxor ferroelectrics that generate small strain and large stress. However, the three ionic conductors mentioned above have a large elastic modulus (> 80 GPa) and relatively low dielectric constant (<100), which places their Q coefficients at least two orders of magnitude above the values predicted by the classical theory.

According to in-situ high-resolution XANES and EXAFS data, oxygen vacancies in Gd-doped ceria induce elastic dipoles, field-induced rearrangement of which is the most probable cause of electrostriction. CeCe-oxygen vacancy (V_o) repulsion increases the CeCe-V_O distance and forms six anomalously short CeCe-oxygen (O_O) bonds. The resulting 7O_O-CeCe-V_O complex behaves as a strong elastic dipole with uniaxial symmetry. An external electric field reduces the CeCe-V_O repulsion, causing reversal of the local distortions. Because of the large strains involved, very large macroscopic stresses, which can reach hundreds of MPa, are generated, in spite of the fact that only a few percent of anion-cation complexes are involved.

Similar to Gd-doped ceria, (Nb, Y)-stabilized cubic Bismuth oxide has a fluorite structure and exhibits large non-classical electrostriction, which monotonically increases within the range of 16-23% of the oxygen vacancies. In the cubic Bismuth oxide, increase in the vacancy concentration from 16 to 23% causes almost 50% decrease in the Young’s modulus, whereas in Gd-doped ceria, increase in the vacancy concentration decreases the Young’s modulus by less than 10%. Similar differences between cubic Bismuth oxide and Gd-doped ceria are observed for Poisson’s ratio: it decreases two fold for the cubic Bismuth oxide and remains unchanged for Gd-doped ceria. These differences indicate that the influence of the large concentration of vacancies on electrostrictive and mechanical properties differ considerably from material to material. This is also supported by the fact that the electrostriction coefficient of 14.5 mol% Y-doped zirconia falls very close to the expected from the classical electrostriction.

Hydrated Y-doped BaZrO_3 is a well-studied protonic conductor in which OH groups can be present at \approx 7% of the oxygen sites. Preliminary investigations indicate that this material also exhibits large non-classical electrostriction; yet hydrated Y-doped BaZrO_3 at room temperature in fact does not contain any vacancies.

On this basis, one can only conclude that a primary condition for large non-classical electrostriction is the presence of a large concentration of point defects, which can be of any type, but which must form elastic dipoles with a particular degree of freedom at room temperature. We suggest that a search for new electromechanically active materials must include those with a large concentration of such point defects in general and, ionic conductors, in particular.