Defect Dipole Enhanced Electromechanical Coupling

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Defect dipoles in oxides can greatly enhance electromechanical coupling when aligned. Defect dipoles form in perovskites, for example, if some B-site cations are replaced with lower valence ions, coupled with neighboring oxygen vacancies. A typical situation would be some Mn^{2+} dopants replacing Ti^{4+}, with neighboring V_O. Defects can have different effects on ferroelectrics, ranging from domain pinning, which can greatly improve the mechanical Q, controlling O-vacancy content to increase material stability, to changes in bulk properties. Here we concentrate on the changes in bulk properties that can be unexpectedly large. We have simulated ferroelectric perovskites such as $BaTiO_3$ as functions of defect dipole concentration and orientations. We have also performed experiments on Mn-doped samples as functions of aging. In an aging process, the defects align spontaneously, whereas in applied fields this process can be better controlled and accelerated. We find that even very small amount of dopants, less than 1%, can cause huge changes in electromechanical response. Since transition metal impurities such as iron can be found in ceramics simply from environmental sources, this effect may also lead to unexplained variability among samples, or lead to ageing effects in nominally undoped samples. Our results are consistent with a long-history of aging studies (Jonker, J. Am. Ceram. Soc. 55, 57, 1972; Ren, Nature Materials 3, 91, 2004). Now we have a detailed microscopic understanding of the effects of defect concentration, distribution and defect dipole alignment on polarization and strain response. We find double hysteresis loops and over 100% increase in piezoelectric strains with small dopant concentrations. Our results are general and should apply to all piezoelectrics with defect dipoles. The single crystal relaxor ferroelectrics such as PMN-PT are already revolutionizing transducer applications. Their main drawback is cost. We see a route towards high coupling ceramics, with boosted response with defect dipole enhanced electromechanical coupling. This work is supported by the US Office of Naval Research and the European Research Council Advanced Grant ToMCaT.