In Situ X-ray Investigation of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Polycrystalline Ceramics in an External Electric Field

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$Pb(Mg_{1/3}Nb_{2/3})O_3$–$x$$PbTiO_3$ (PMN–PT) is a solid solution of a prototypic relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ with ferroelectric $PbTiO_3$. A morphotropic phase boundary (MPB) exists in the PMN-PT phase diagram at x≈0.30, and anomalously high dielectric and piezoelectric properties have been reported for near-MPB compositions in single crystals.[1,2] The mechanism known as polarization rotation may be responsible for the enhanced polarizability and piezoelectricity; it has been observed in single crystals indirectly (by strain-electric field measurements) and directly (by X-ray and neutron diffraction investigations).[3,4] However, large single crystals are normally unavailable or costly, and applications often rely on more easily produced polycrystalline materials. For example, bulk PMN-0.30PT ceramics have been used in sensors and actuators due to high piezoelectric coefficients, and in electrocaloric cooling devices due to high polarizability and polarization.[5,6] An understanding of the underlying physics of these properties in polycrystalline PMN-0.30PT is not fully developed.

In order to determine the structural responses to electric fields at global and local scales, *in situ* X-ray diffraction and pair distribution function (PDF) techniques were employed on bulk polycrystalline PMN-0.30PT. *In situ* diffraction patterns under electric fields show continuous Bragg peak changes, e.g. peak shape, position, and splitting. The Le Bail fitting method was used to determine the crystal structure at different field stages, and a *Cm* (monoclinic M_A) to *Pm* (monoclinic M_C) to *P*4*mm* (tetragonal) crystal structure change with increasing field was evidenced. This transition sequence can be explained by the polarization rotation mechanism, which has only been experimentally shown in PMN-PT single crystals, but not yet in polycrystalline materials. Since PMN-PT is a challenging system due to its high degree of complexity and local structure distortions, *in situ* PDF measurements were performed to characterize the structure of PMN-0.30PT at the local scale. Refinements of a model using the full PDF profile show monoclinic *Cm* can also best describe the local structure of unpoled ceramics. As increasing electric fields are applied, a systematic change of the PDF is observed, confirming a continuous change in the structure of the monoclinic phase. The local structure transformed into *P*4*mm* tetragonal at the highest fields. The local scale observations via PDF provide more evidence of the polarization rotation mechanisms active in polycrystalline PMN-0.30PT.

Reference:

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