Effect of Ru Doping on the Domain Structure and Macroproperties of PbZn1/3Nb2/3O3-PbTiO3 near the Morphotropic Phase Boundary

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The search for novel multifunctional materials over the past two decades has spotted complex perovskite-type ferroelectric materials of the general formula ABO₃, with Pb²⁺ in the A-site and various transition elements in the B-site. Among them solid solutions of canonical relaxor ferroelectrics (showing no long-range ferroelectric ordering below the temperature of the dielectric maximum) and normal ferroelectrics are of particular technological importance because of the huge electromechanical coupling and strong photoelastic effects near the morphotropic phase boundary. Our understanding of the relationship between the nano-scaled domain structure and the outstanding macroproperties of these materials is still a challenging problem. Coexistence of several phases and a strong deviation of the local structure from the overall, average structure are typical of this type of materials. We applied atomic and piezoresponse force microscopy (AFM/PFM), dielectric measurements, X-ray diffraction analysis and Raman scattering to study the ferroelectric domains and properties of single crystals of pure and Ru-doped 0.9PbZn_{1/3}Nb_{2/3}O₃-0.1PbTiO₃. The system $(1-x)PbZn_{1/3}Nb_{2/3}O_3-xPbTiO_3$, x $\sim 0.09 - 0.11$ shows the strongest ever recorded direct and converse piezoelectric effect. On the other hand, Ru is a mixed-valence photochromic element and its addition to complex oxides, including perovksites, enhances the photorefractive effect close to the red and near-infrared spectral range, which is of significant interest for optical memories. AFM/PFM images reveal the existence of tetragonal and non-tetragonal ferroelectric domains in $0.9PbZn_{1/3}Nb_{2/3}O_3$ -0.1PbTiO₃, which has not been directly observed so far. The dielectric and elastoelectric loops show that Ru doping, Ru/(Ti+Zn+Nb) ~ 0.002, leads to significant ferreoelectric hardening due to the immobilization of domain walls. Besides, the addition of Ru decreases the ferroelectric domain size, reduces the polar fraction distributed in the pseudo cubic matrix and also changes the unit cell parameters of the overall tetragonal structure.

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