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Transformation processes in relaxor ferroelectric $PbSc_{0.5}Ta_{0.5}O_3$ heavily doped with Nb and Sn

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Abstract. The effect of a third type of B-site cation on the temperature- and pressure-induced structural changes in ABO_3-type relaxors has been studied by in-situ Raman scattering and X-ray diffraction on $0.72PbSc_{0.5}Ta_{0.5}O_3-0.28PbSc_{0.5}Nb_{0.5}O_3$ (PSTN) and $0.78PbSc_{0.5}Ta_{0.5}O_3-0.22PbSnO_3$ (PSTS). The incorporation of Nb into the PST matrix is an isovalent substitution for Ta^{5+} on the ferroelectrically active B-site, whereas the incorporation of Sn^{4+} is a coupled aliovalent substitution for both types of B-cations in the host system. Both PSTN and PSTS exhibit the characteristic temperature T^*, which for PSTS is shifted to slightly lower temperatures. The incorporation of Nb and Sn into the PST matrix smears the transformation processes near and below T^* and suppresses the ferroelectric long-range order at low temperatures. Both PSTN and PSTS exhibit a continuous pressure-induced phase transition. The high-pressure phases have the same structural features as for pure PST: suppressed B-cation off-centre shifts, enhancement of coupled Pb–O ferroic species, and long-range order of anti-phase tilts of the BO_6 octahedra. Nb-doping shifts the critical pressure p_c from 1.9 GPa for pure PST to 2.5 GPa, whereas Sn-doping lowers p_c to 1.3 GPa. The incorporation of both Nb and Sn decreases the degree of the overall pressure-induced structural distortion, with the effect of Sn being more pronounced than Nb. The dilution of the B-site cation system with Sn^{4+} results in local electric and elastic fields which reduce the coherence between nanoregions with anti-phase octahedral tilting and shifts the pressure at which long-range order of the tilts occurs to ~4 GPa.

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Introduction

Perovskite-type (ABO_3) relaxor ferroelectrics exhibit remarkably large dielectric permittivities near room temperature and strong structural inhomogeneities on the nanometre scale [1]. Exceptionally high piezoelectric and electro-optic responses have been detected in solid solutions of Pb-based relaxors (Pb occupying the A-position of the perovskite-type structure) and $PbTiO_3$ [2], whose local structure closely resembles the nanoscale atomic arrangements of relaxors [3]. To better understand the intrinsic structural features of relaxors and hence the structure-property relationships, temperature- as well as pressure-induced structural transformations have been extensively studied by X-ray and neutron diffraction [4–9], pair-distribution-function analysis [10, 11], quasielastic [12] and inelastic neutron scattering [13], Raman and infrared (IR) spectroscopy [14–17], Brillouin spectroscopy [18], nuclear magnetic resonance [19], X-ray absorption spectroscopy [20, 21], piezoresponse force microscopy [22, 23], acoustic emission [24] and dielectric measurements [25–28]. It is currently accepted that the broad frequency-dispersive peak of the dielectric permittivity as a function of temperature, which is a unique property of relaxors, is due to the existence of dynamic polar nanoregions (PNRs) flipping between different orientation states, each of which corresponds to one of the possible crystallographic directions along which the cubic unit cell can be distorted corresponding to a polar class. PNRs have been directly observed by high resolution transmission electron microscopy [29] and in diffraction experiments their presence can be deduced from diffuse scattering streaks along the $\langle 110 \rangle^*$ directions [4, 5]. PNRs nucleate at the so-called Burns temperature T_B, which is hundreds of kelvins above the temperature of the dielectric permittivity maximum T_m [30]. On further cooling, at $T^* < T_B$ PNRs enlarge and slow down due to increased coherence between the initially-formed polar species [14, 31] and finally evolve into normal (long-range ordered) ferroelectric domains at the