Structural peculiarities in (1-x)$Na_{0.5}Ba_{0.5}TiO_3$-$x$$BaTiO_3$ at the morphotropic phase boundary studied by high-pressure XRD and Raman spectroscopy

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Perovskite-type (ABO_3) ferroelectric solid solutions are widely used functional materials, whose properties are utilized, for example, in sensors and actuators. The currently market-leading ferroelectric ceramics $Pb_{1-x}Zr_xTiO_3$ contain lead, which is undesirable from an environmental point of view. The solid solution $Na_{0.5}Bi_{0.5}TiO_3$-$x$$BaTiO_3$ (NBT-xBT) is one of the promising lead-free alternatives, however, its properties still need to be accurately constrained. Compositional variations may change the symmetry of the ferroelectric phase and shape the nanoscale structure, allowing to tune the properties by chemical substitutions. At the morphotropic phase boundary (MPB) with x = 0.05 - 0.06 for NBT-xBT the dielectric permittivity, piezoelectric coefficient, and electromechanical coupling factor are enhanced (Ge at al. 2011) due to an increased structural flexibility (de la Flor et al. 2019), making such compositions a good starting point for improvement by additional chemical doping. For an effective modification of the material, better understanding of the relation between the chemical composition and the nanoscale structural features in NBT-xBT is needed.

In this study, we have analyzed the response of the structure of NBT-0.048BT to external hydrostatic stress by performing high-pressure single-crystal X-ray diffraction (XRD) and Raman spectroscopic experiments up to 9 GPa, using the diamond-anvil-cell technique. It is known that in the case of Pb-based relaxor ferroelectrics pressure suppresses the polar order, while it enhances the antiferrodistortive order. Thus, the complementary high-pressure analyses of Bragg scattering, informative of long-range order, X-ray diffuse scattering (XDS), indicative of intermediate-range order and Raman scattering, sensitive to the intermediate-/short-range order can help to reveal subtle structural features, which are hard to detect at ambient pressure (Mihailova et al. 2011). The combination of different experimental methods allows us to obtain a comprehensive picture of the pressure-induced structural transformations ranging from the local to the long-range scale. At ambient and low pressure the deviations from the average pseudo-cubic perovskite structure produce strong diffuse scattering, which evolves into sharp Bragg peaks with increasing pressure [see Fig. 1 (a) and (c)]. The appearance of additional Bragg peaks indicates a phase transition between 4.4 and 5.5 GPa. The Raman data [Fig. 1 (b) and (d)] resolve the multistep local scale structural changes that lead to the change in symmetry. First a reduction of the Ba-induced local BO_6 anisotropy is taking place at 0.5 - 0.9 GPa, followed by decoupling of adjacent A- and B-site dipoles near 1.2 GPa. This allows for development of antipolar order of A-cation off-center displacements starting above 1.9 GPa, similar as it has been observed by Kreisel et al. (2003) in pure NBT at lower pressures. Furthermore, there is a strong amplification and increase in correlation length of octahedral tilts above 2.7 GPa and a change in the tilt pattern at 4 - 4.5 GPa.

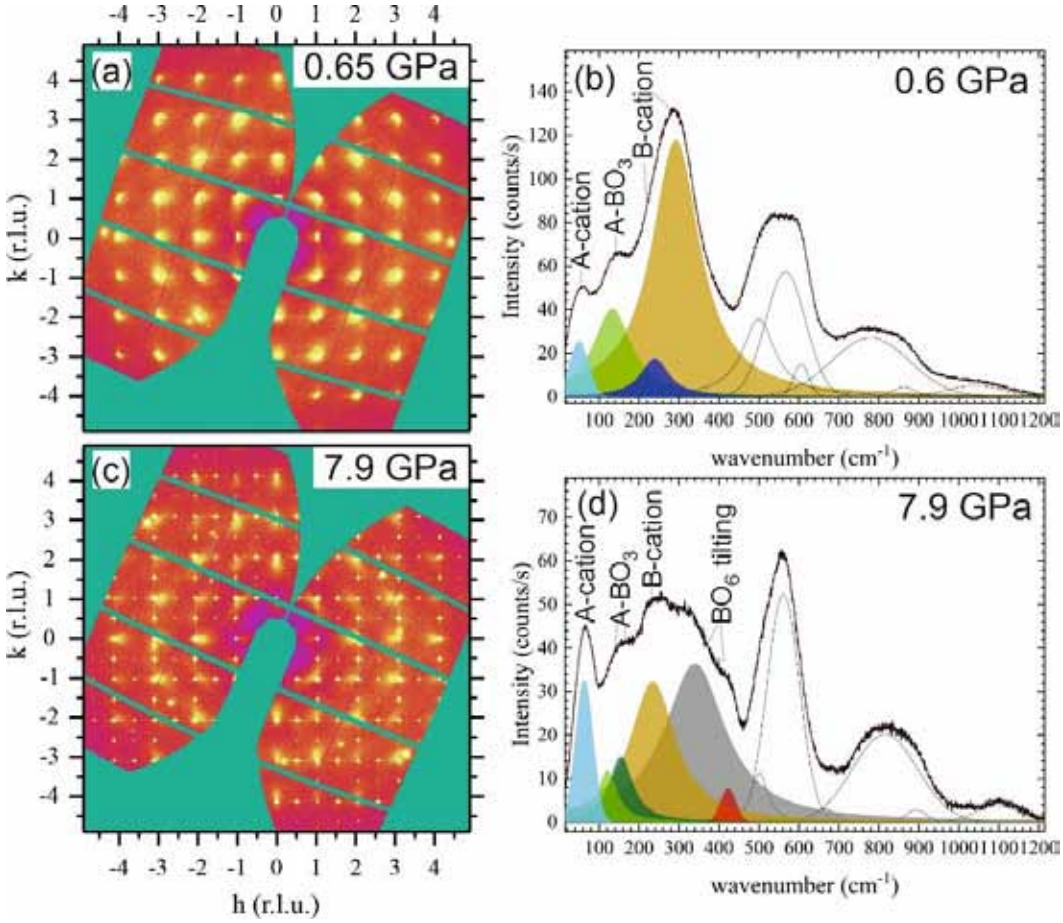

Figure 1. X-ray diffraction pattern in *hk*0 plane (a) and (c) and Raman scattering (b) and (d) of NBT-0.048BT at ~0.6 GPa and 7.9 GPa. The colored peaks in (b) and (d) are associated with A-cation off-centering vibrations (light blue), A-BO_3 translations (light and dark green), B-cation off centering vibrations (dark blue and orange) and BO_6 tilting vibrations (grey and red).

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