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Structural investigations on lead-free $Bi_{1/2}Na_{1/2}TiO_3$-based piezoceramics

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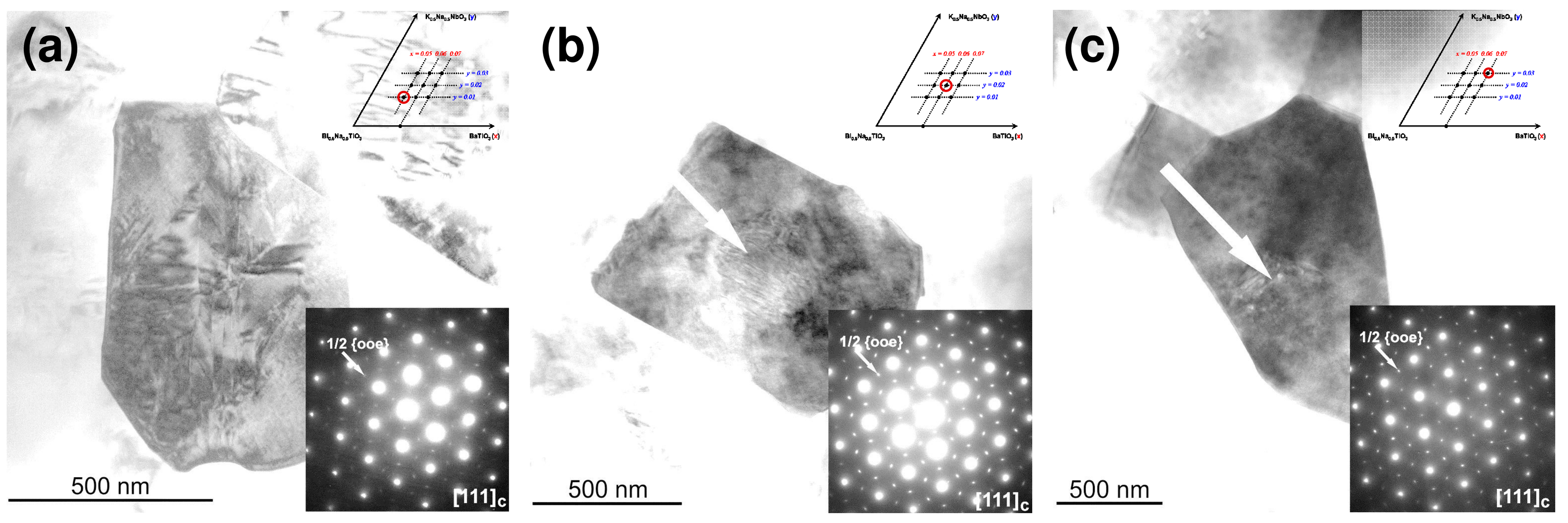
Project B3

Motivation

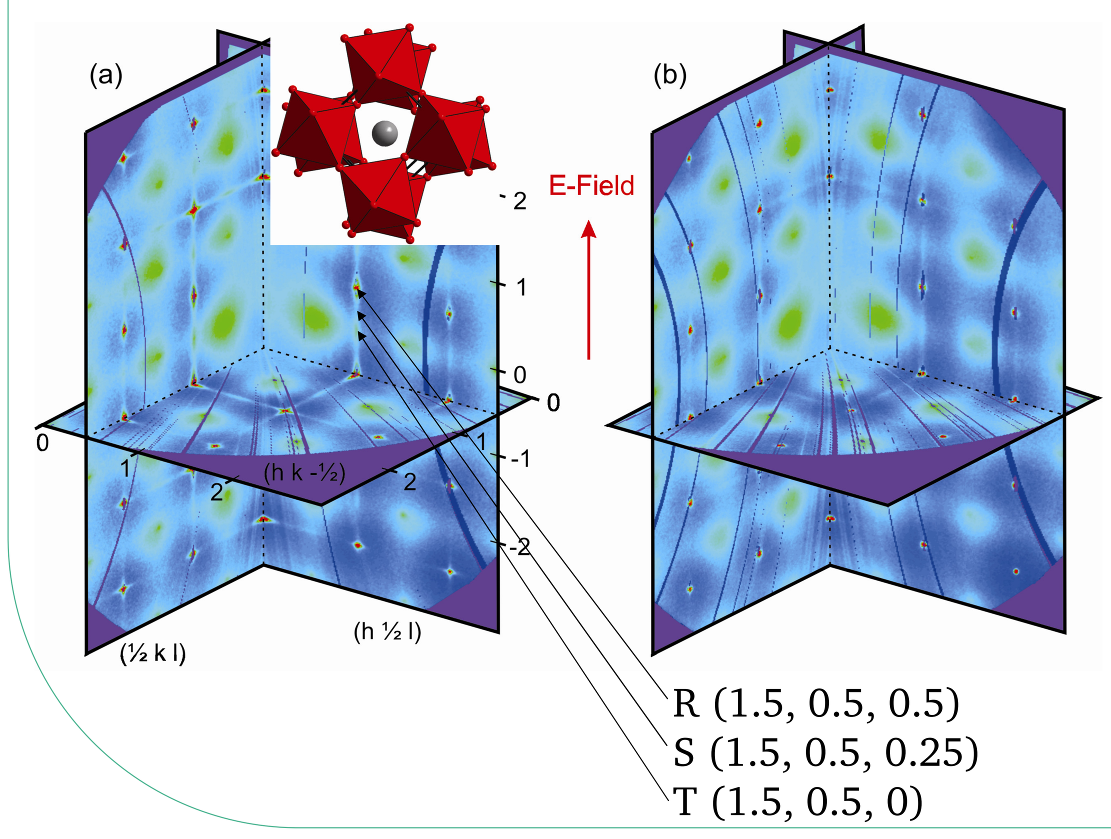
During the last funding period, the structure evolution of lead-free piezoceramics with emphasis on the quasi-binary (1-x)$Bi_{1/2}Na_{1/2}TiO_3$-x$BaTiO_3$ (BNT-BT, BNT-100xBT) and quasi-ternary (1-x-y)$Bi_{1/2}Na_{1/2}TiO_3$-x$BaTiO_3$-y$K_{0.5}Na_{0.5}NbO_3$ (BNT-BT-KNN, 100(1-x-y)-100x-100y) system was investigated. Samples were characterized by combining transmission electron microscopy (TEM), X-ray and neutron diffraction and scattering as a function of composition, and electric field.

TEM of BNT-BT-KNN



Bright field (BF) TEM micrographs of (a) 94-05-01, (b) 92-06-02 and (c) 90-07-03 in the initial state along pseudo cubic [111] zone axis. Sample 94-05-01 shows grains with domain contrast, whereas in 92-06-02 and 90-07-03 a core-shell structure is present (marked with arrows). Corresponding selected area electron diffraction (SAED) patterns are shown in the insets. Along the [111] zone axis ½(ooe) superlattice reflections (SR) are visible. Both types of SR, ½(ooo) and ½(ooe), are present in all investigated compositions, although with different intensity.

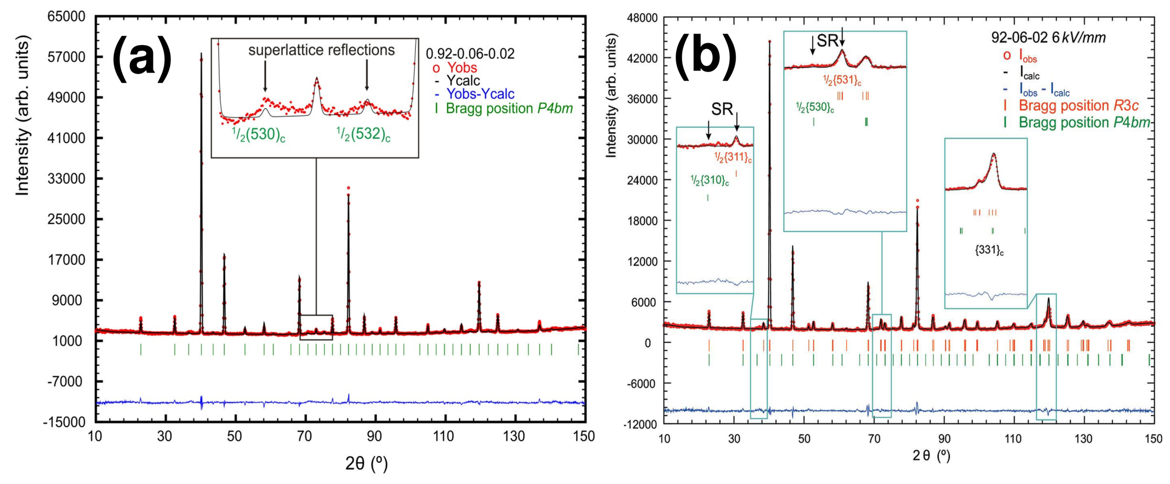
In situ diffuse X-ray scattering of BNT-BT



Diffuse X-ray scattering images of BNT-04BT (a) in the initial state and (b) under an applied field of 4.6 kV/mm. The inset in (a) shows the $a^-a^-a^-$ octahedral tilt system giving rise to the R-type SR at ½(ooo). A reduction of the diffuse intensity between these reflections under applied field is clearly visible in (b). Curved streaks are caused by detector saturation errors.

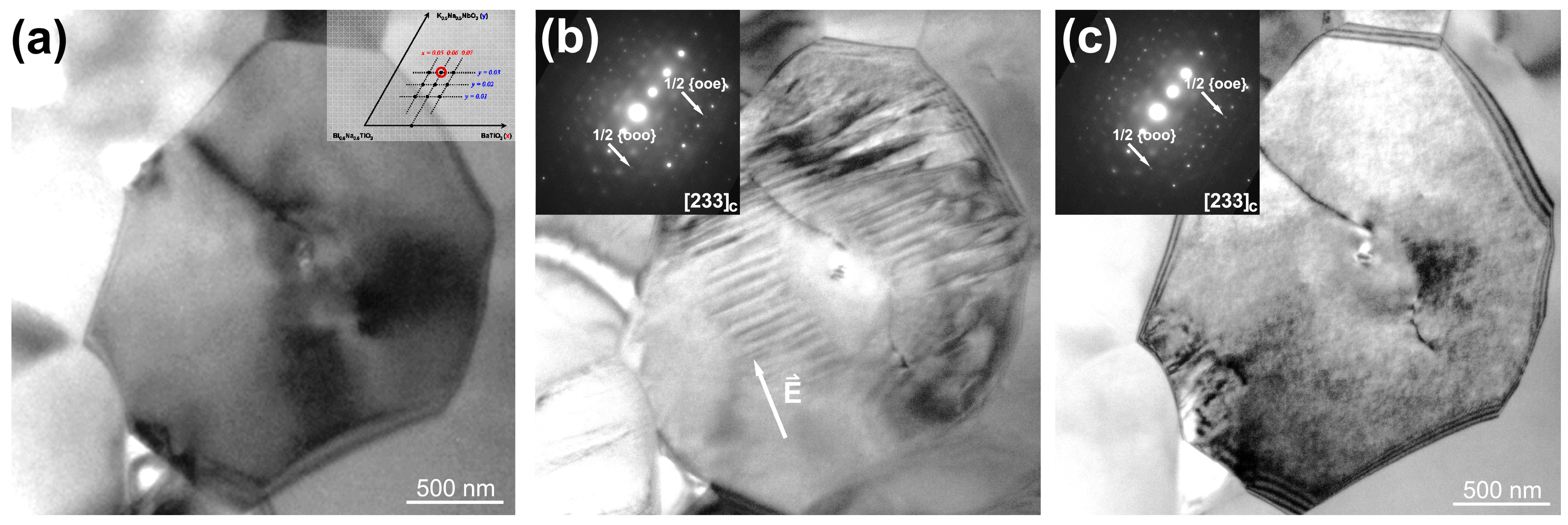
Results

In situ neutron diffraction of BNT-BT-KNN



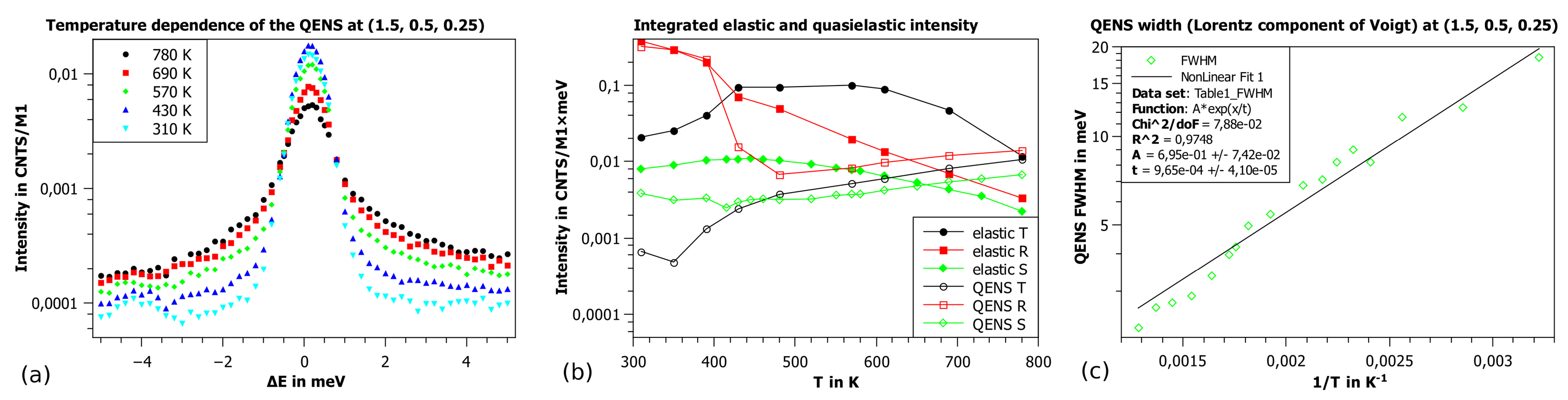
Rietveld refined neutron diffraction data of sample 92-06-02. (a) In the initial state ½(ooe) SR are present. (b) Under an electric field a phase transformation from the tetragonal P4bm to the rhombohedral R3c phase occurred.

In situ TEM of BNT-BT-KNN



Sample 91-06-03 (a) BF micrograph showing one grain with homogenous contrast prior to electric field application. (b) Grain under an applied electric field of about +/–5 kV/mm. Formation of lamellar domains is visible. Both SR are present (shown in the inset). (c) Removing the electric field the visible domain configuration vanishes. A reversible electric-field induced phase transformation in the ternary system BNT-BT-KNN from tetragonal P4bm to rhombohedral R3c phase was verified by means of *in situ* electron microscopy [1] and neutron-diffraction experiments [D].

Quasielastic neutron scattering of BNT-BT



The quasielastic neutron scattering (QENS) in BNT-04BT exhibits a strong temperature dependence at the S point (a,b), but also at the R and T points (b). The temperature dependence at these three points is fundamentally different up to ~550 K, which corresponds to the temperature of the permittivity maximum. Also shown in this plot is the intensity of the elastic line. Here, the crossover of the R point and T point intensity around 430 K is particularly significant, since it is close to the depolarisation temperature of the unpoled material. (c) The width of the QENS component at the S point approximately follows an Arrhenius law. Remarkably, the temperature dependence is inverted, i.e. the activation energy appears to be negative. This unusual behaviour can possibly be explained by complex lattice-phonon interactions at the nanoscopic phase boundaries.

Publications last funding period

1) L.A. Schmitt, J. Kling, M. Hinterstein, M. Hoelzel, W. Jo, H.-J. Kleebe. “Structural investigations on lead-free $Bi_{1/2}Na_{1/2}TiO_3$-based piezoceramics”. J. Mater. Sci. **46**, 4368-4376 (2011).

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5) M. Hinterstein, J. Rouquette, J. Haines, Ph. Papet, M. Knapp, J. Glaum, H. Fuess. “Structural Description of the Macroscopic Piezo- and Ferroelectric Properties of Lead Zirconate Titanate”. Phys. Rev. Lett. **107**, 077602 (2011).

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7) E.-M. Anton, L.A. Schmitt, M. Hinterstein, J. Trodahl, B. Kowalski, W. Jo, H.-J. Kleebe, J. Rödel and J.L. Jones. “Structure and temperature-dependent phase transitions of lead-free $Bi_{1/2}Na_{1/2}TiO_3$-$Bi_{1/2}K_{1/2}TiO_3$-$K_{0.5}Na_{0.5}NbO_3$ piezoceramics”. J. Mater. Res. **27** (19), 2466-2478 (2012).

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10) I. Levin, I.M. Reaney, E.-M. Anton, Wook Jo, J. Rödel, J. Pokorny, L.A. Schmitt, H.-J. Kleebe, M. Hinterstein and J.L. Jones. “Local Structure, Pseudo-Symmetry, and Phase Transitions in $Na_{1/2}Bi_{1/2}TiO_3$-$K_{1/2}Bi_{1/2}TiO_3$ Ceramics”. Phys. Rev. B **87**, 024113 (2013).

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12) L.A. Schmitt, D. Schrade, H. Kungl, B.-X. Xu, R. Mueller, M.J. Hoffmann, H.-J. Kleebe and H. Fuess. “Bimodal domain configuration and wedge formation in tetragonal $Pb[Zr_{1-x}Ti_x]O_3$ ferroelectrics”. Comput. Mater. Sci. **81**, 123-132 (2014).

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14) L.A. Schmitt, H. Kungl, M. Hinterstein, L. Riekehr, H.-J. Kleebe, M. J. Hoffmann, R.-A. Eichel and H. Fuess. “The Impact of heat treatment on the Domain Configuration and Strain Behavior in Pb(Zr, Ti)O_3 Ferroelectrics”. J. Am. Ceram. Soc., accepted (2014).

5 Key Publications (2003-2014)

A. L.A. Schmitt, K.A. Schönau, R. Theissmann, H. Fuess, H. Kungl, M.J. Hoffmann. “Composition dependence of the domain configuration and size in $Pb(Zr_{1-x}Ti_x)O_3$ ceramics”. J. Appl. Phys. **101**, 074107 (2007).

B. K.A. Schönau, L.A. Schmitt, M. Knapp, H. Fuess, R.-A. Eichel, H. Kungl, M.J. Hoffmann. “Nanodomain structure of $Pb[Zr_{1-x}Ti_x]O_3$ at its morphotropic phase boundary: Investigations from local to average structure”. Phys. Rev. B **75**, 184117 (2007).

C. L.A. Schmitt, H.-J. Kleebe. “Single Grains Hosting Two Space Groups: A Transmission Electron Microscopy Study of a Lead-Free Ferroelectric”. Funct. Mater. Lett. **3**, 55-58 (2010).

D. M. Hinterstein, M. Knapp, M. Hölzel, W. Jo, A. Cervellino, H. Ehrenberg, H. Fuess. “Field-induced phase transition in $Bi_{1/2}Na_{1/2}TiO_3$-based lead-free piezoelectric ceramics”. J. Appl. Crystallogr. **43**, 1314-1321 (2010).

E. J.E. Daniels, W. Jo, J. Rödel, D. Rytz, W. Donner. “Structural origins of relaxor behavior in a 0.96$(Bi_{1/2}Na_{1/2})TiO_3$-0.04$BaTiO_3$ single crystal under electric field”. Appl. Phys. Lett. 98, 252904 (2011).