

MS17 O1

Structural reaction of PZT under *in situ* conditions using Synchrotron powder diffraction - influence and stability of nanostructures Hartmut Fuess^a, Kristin A. Schoenau^a, Ljubomira A Schmitt^a, Michael Knapp^b, Matteo Leoni^c, Mario Maglione^d ^aMaterials Science, Darmstadt University of Technology, Germany. ^bCELLS, Barcelona, Spain. ^cDept. Materials Engineering and Industrial Technologies, University of Trento, Italy. ^dICMCB-CNRS, Université Bordeaux I, France.
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Ferroelectric lead zirconate titanate, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT), is currently used in a wide range of applications converting electrical into mechanical energy. Highest strains and piezoelectric properties are found at the so-called morphotropic phase boundary (MPB) between tetragonal and rhombohedral symmetry. Previous results describe the structure at the MPB as monoclinic [1], whereas our recent studies using high-resolution synchrotron x-ray powder diffraction in combination with TEM and EPR [2, 3] were able to correlate XRD observation with a nanodomain structure. The internal symmetry of the nanodomains is difficult to determine due to strong coherence effects in diffraction experiments, which is in correspondence with findings for relaxor ceramics using martensitic theory [4]. The stability field of these nanodomain structures is strongly dependent on sample composition, temperature and electric field. *In situ* synchrotron diffraction experiments in transmission mode at the beamline B2, HASYLAB, Hamburg, reveal changes related to these three parameters. Furthermore, the microstructural reaction of the material is investigated under operating conditions. While the domain structure of samples with low nanodomain content is changed under electric field into that of the adjacent tetragonal or rhombohedral phase field, samples with a distinct balance between Zr-content and tetragonal c/a-ratio show stable nanodomains. These samples undergo reversible phase transitions between a mixture of tetragonal microdomains and nanodomains at the coercive field and rhombohedral microdomains at high voltage. *In-situ* electric field diffraction above the transition temperature between nanodomain structures and the tetragonal phase show tetragonal domain switching. Furthermore, temperature dependent measurements of the dielectric constant are able to clarify the character of the ferroelectric-to-paraelectric transition and gives new information on the behavior of nanodomain structures under field. This enables us to correlate properties of this material with the relaxor systems PMN-PT and PZN-PT.

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MS17 O2

Insights into thermoelectric candidate materials from powder diffraction. Birgitte L. Pedersen^a, Henrik Birkedal^a, Eiji Nishibori^b, Poul Toft Frederiksen^c, Bo Brummerstedt Iversen^a. ^aDepartment of Chemistry & Interdisciplinary Nanoscience center, University of Aarhus, Denmark. ^bDepartment of Applied Physics, Nagoya University, Japan. Grundfos A/S, Bjerringbro, Denmark.
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The β -phase of p-type semiconductor Zn_4Sb_3 has attracted attention because it is a potential candidate for thermoelectric purposes in the intermediate temperature range (473-673 K) [1, 2]. The thermoelectric Figure of Merit is defined as $ZT = TS^2\sigma/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature. Although Zn_4Sb_3 exists in at least three crystalline phases, only the β -phase, stable from 263-765 K, has high thermoelectric performance [1-3]. The origin of the outstanding properties is the presence of interstitial zinc sites creating a highly defect crystal structure, which effectively lowers thermal conductivity, while preserving electronic conduction [4, 5]. Below 263 K, Zn_4Sb_3 undergoes two phase transitions to Zn-ordered highly complicated phases [6]. The combination of interstitial disorder and highly complex low temperature phases makes the crystallographic characterization of these materials challenging.

To become commercially applicable, it is crucial that the material is compactable and stable during thermal cycling and that it has the highest possible thermoelectric performance. Previous studies have shown that ZT can be improved by doping with Cd.[7] To understand and optimize the effect of doping, knowledge about the dopant atom siting is essential. We present and discuss the use of powder diffraction for the analysis of these complicated materials that represent true characterization challenges. Sample compaction, a key processing step for the use of these microcrystalline materials, may change the purity and also influence the performance of the materials [8]. As even small levels of impurities can have a profound effect on performance, high quality powder diffraction data is crucial.

We discuss the question of dopant atom location by using high resolution synchrotron powder diffraction on a slightly mercury doped sample, $\text{Hg}_{0.04}\text{Zn}_{3.96}\text{Sb}_3$. Thermal stability and decomposition pattern has been studied on a pure and a Te-doped sample by multi temperature synchrotron powder diffraction. Te-doping clearly changes the decomposition pattern, and although no immediate thermal stabilization was achieved, the study suggests that doping might be a way to stabilize the system.

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