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Investigation of the domain structure, size and orientation in lead zirconate titanate PZT ceramics by transmission electron microscopy

L.A. Schmitt[a], K.A. Schoenau[a], R. Theissmann[a],
M. Knapp[a,b], H. Kungl[c], H. Fuess[a]

[a]*Institute for Materials Science, Darmstadt University of Technology, Petersenstr. 23, 64285 Darmstadt, Germany* [b]*CELLS, P.O.B 68, 08193 Barcelona, Spain* [c]*Institute of Ceramics in Mechanical Engineering, IMK Zentrallaboratorium, Haid-und-Neu-Str. 7, University of Karlsruhe, D-76133 Karlsruhe, Germany. E-mail: Ljuba@st.tu-darmstadt.de*

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Undoped stochiometric PZT samples, $Pb(Zr_xTi_{1-x})O_3$, with different Zr/Ti ratios in a composition range from x = 0.60 to x = 0.45 across the morphotropic phase boundary (MPB) were prepared by the conventional mixed-oxide route from PbO, ZrO_2 and TiO_2 powders. A fundamental study of the local domain structure and orientation was carried out. The observed domain configurations were compared to the one theoretically predicted by Sapriel [1], Fousek and Janovec [2]. The domain structure of the range of samples investigated is strongly composition dependent. Compositions belonging to the tetragonal (45/55) and rhombohedral (60/40) phase field, not close to the MPB, show the appearance of a bimodal domain configuration with alternating latitudes. Around the morphotropic phase boundary a decrease in bimodal distribution is observed, accompanied by an increase in domain width and nanodomain formation within the large microdomains. In-situ hot-stage TEM experiments revealed domain wall motions and the appearance of domains at nanoscale during recooling. ESEM examinations have been undertaken as a complementary method to confirm the TEM experiments. The electronmicroscopical results were compared to high-resolution synchrotron X-Ray powder diffraction data measured at different temperatures in transmission geometry. In order to directly visualize the theoretically described domain switching process [3], additional in-situ electric-field TEM experiments are in preparation.

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New One-Dimensional Phases in the Sr/Ca-Mn/Co-O System

Khalid Boulahya, M. Parras, J.M. González-Calbet

Depto. de Química Inorgánica I, UCM, 28040-Madrid, E-mail: Spain.khalid@quim.ucm.es

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One-dimensional oxides formed by the intergrowth between the 2H-$BaNiO_3$ (1) and the K_4CdCl_6 (2) structural types are in the limelight due to their exciting structural physico-chemical properties. The former is built up of isolated chains of $[BO_6]$ octahedra sharing faces running along the *c*-axis. The latter, also formulated as $A_3(A'B)O_6$, shows similar features but the chains are now formed by alternating octahedra (O_h) and trigonal prismatic (TP) units sharing common faces in a 1:1 stacking sequence. Intermediate phases have been reported, all of them defined by the formula $(A_3A'BO_6)_\alpha\,(A_3B_3O_9)_\beta$ (3) where B stands for cations in O_h coordination and A' refers to cations in TP environment. We report in this paper new phases in the Sr/Ca-Mn/Co-O system.

The $\alpha=2$, $\beta=1$ term, showing the polyhedra sequence of two O_h and one TP along c-axis, has been reported for $Sr_4Mn_2CoO_9$ (4). Partial substitution of Sr by Ca leads to the stabilization of new members of the above mentioned series, some of them presenting some structural peculiarities. This is the case for $Sr_3CaMn_2CoO_9$, isotypic to $Sr_4Mn_2CoO_9$ that introduces some structural strain, since twin planes are observed by HREM. When Ca substitution increases, the number of octahedra between prisms in the polyhedra sequence decreases. This is the case of $Sr_9Ca_9Mn_8Co_5O_{39}$, showing a complex sequence of O_h and TP.

This structure is formed by a complex intergrowth of structural blocks of the $\alpha=2$, $\beta=1$ member, 2Oh-1TP, alternating with the $\alpha=1$, $\beta=1$ (1Oh-1TP) ones, in an ordered way, leading to 2Oh-1TP-2Oh-1TP-1Oh-1TP-2Oh-1TP-1Oh-1TP- polyhedra sequence.

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