

ically, produced by external fields there are 10 types of configurations with non-zero average polarization. It appears that electric field, possibly in combination with mechanical stress, may induce 7 non-equivalent coherent configurations formed each by equivalent domain states with same free energy in the field(s). The form of average tensor properties is given by the corresponding effective symmetry.

By examining tensor properties of the coherent configurations (CC's) we establish five cases where additional relationships between tensor components exist for certain material properties, compared to what is usually obtained for single domain crystals with same macroscopic symmetry. In one case even the stabilizer of each polar tensor of even rank differs from common expectations.

For representative CC's we specify average material tensors up to rank 4 in terms of tensor components of the same selected state.

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Keywords: engineered domain configurations, effective symmetry, average tensor properties

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Lattice Parameters of the PZT 90/10 Ceramic doped with La

Paweł Pacek^a, Joanna Skrzypek^b, Krystyna Wokulska^a, ^a*Institute of Materials Science, University of Silesia, Poland.* ^b*Department of Materials Science, University of Silesia, Poland.* E-mail: p_pacek@o2.pl

The PZT ceramics have been attracting with considerable attention in a number of different context. One of them are their ferroelectrical properties.

Sample of $\text{Pb}_{0.94}\text{La}_{0.06}\text{Zr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ was prepared by sol-gel process and sintered at 1200°C for 2 hours.

Investigation lattice parameters of the specimen were studied using X-ray diffraction (XRD). X-ray traces were recorded using a Phillips diffractometer between 20°-110° (CuK α radiation) with scan step of 0.02° and scan time 14s/step.

In agreement with phase diagram for PLZT system [1] our sample should have a tetragonal structure. To confirm that assumption we prepared two simple simulated scans for tetragonal and rhombohedral structure. On the basis of the results and other data [2] we agreed with that assumption and made preliminary analysis of lattice parameters in profile matching mode. As a results of our investigation we obtained a following parameters: $a=b=4,1051\pm 0,0007\text{Å}$, $c=4,1194\pm 0,0005\text{Å}$.

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Keywords: ferroelectrics, ceramic materials, powder X-ray diffraction

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Structural Phase Transitions and Hydrogen bonding in $\text{Rb}_3\text{H}(\text{SO}_4)_2$

Diptikanta Swain, T.N. Guru Row, *Solid State and Structural Chemistry Unit., Indian Institute of Science, Bangalore-560 012.* E-mail: diptikanta@sscu.iisc.ernet.in

Compounds of the type $\text{A}_3\text{H}(\text{XO}_4)_2$, where $\text{A} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$, $(\text{NH}_4)^+$ and $\text{X} = \text{S}, \text{Se}$ are known ferroelectric and paraelectric materials. Recently, structural phase transition in $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ have been studied in detail [1]. We have investigated the phase transition in the analogous $\text{Rb}_3\text{H}(\text{SO}_4)_2$, the structure of which at room temperature was determined by Fortier *et al.*[2]. in 1985, at four different temperatures to follow the phase transition behavior. The data were collected on a Bruker Smart Apex CCD system equipped with an

Oxford cryostat at 293K, 100K, 393K and 425K respectively. The hydrogen atom is localized at the midpoint at 100K with respect to the sulfate tetrahedra while at room temperature it is connected with one of the oxygen atoms. DSC studies on a single crystal of the compound indicate phase transitions around 399K and 425K. The crystal structures of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ at four different temperatures show subtle conformational and packing changes and the geometry around the Rb atoms shows different coordination with respect to temperature.

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Keywords: phase transition, hydrogen bonding, coordination

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Relaxor Ferroelectric Behaviour of $\text{Ba}_{1-x}\text{A}_x(\text{Ti}_{0.7}\text{Zr}_{0.3})\text{O}_3$ Compositions ($\text{A}=\text{Ca},\text{Sr}$)

Kamel Taïbi^a, A. Kerfah^a, A. Guehria-Laïdoudi^a, A. Simon^b, J. Ravez^b, ^a*Laboratoire de Cristallographie Thermodynamique, Faculté de Chimie, U.S.T.H.B., B.P 32 B.E.Z Alger, Algeria.* ^b*I.C.M.C.B.-C.N.R.S., Université de Bordeaux I, 87 avenue du Dr A. Schweitzer, 33608 Pessac, France.* E-mail: taibikameldz@yahoo.fr

The relaxor ferroelectric materials exhibit a large range of interesting properties related to their complex order/disorder nanostructures. The relaxor behaviour is well known in lead based compositions. Nevertheless, the latter present a disadvantage due to the toxicity of polluting substances. The actual evolution of research is directed to replace the lead by lead-free compositions [1, 2]. The aim of the present work was to prepare and to characterize some ceramics derived from BaTiO_3 by cationic substitution in the 12-C.N crystallographic site.

The various compositions were obtained by solid state synthesis. Room temperature X-ray diffraction analysis allowed us to determine the limits of solid solution. Dielectric measurements exhibit a relaxor behaviour in the range $0 < x < 0.20$. Whatever A, T_m decreases as x increases. However, the decrease was comparatively lower in the case of the calcium substitution. This result is related to the size of each cation. For the Ba-Sr substitution the decrease of T_m results from reduction of the c/a ratio. On the contrary, for the Ba-Ca substitution, Ca^{2+} induces a local polar moment leading to a small decrease of T_m . Concerning the strontium substitution, one of the noteworthy characteristic is the very high value in the maximum of ϵ'' .

[1] Ravez J., Simon A., *J. Korean Phys. Soc.*, 1998, **32**, 955. [2] Nagata H., Takeda T., *Spn. S. Appl. Phys.*, 1998, **37**, 5311

Keywords: ferroelectric relaxors , lead free materials , disordered materials

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Ferroelectric Phase Transition Mechanism in $\text{C}_5\text{H}_6\text{NBF}_4$ by X-ray Crystal Analysis

Hirofumi Kasatani, *Department of Materials and Life Science, Shizuoka Institute of Science and Technology, 2200-2 Toyosawa, Fukuroi, Shizuoka, Japan.* E-mail: kasatani@ms.sist.ac.jp

Pyridinium Tetrafluoroborate $\text{C}_5\text{H}_6\text{NBF}_4$ (abbreviated to PyBF_4) undergoes a ferroelectric-paraelectric phase transition at $T_1=238.7\text{K}$, and another phase transition at $T_2=204\text{K}$ [1, 3]. From the NMR studies [2], the pyridinium and tetrafluoroborate ions were the dynamical disorder state at room temperature. It was suggested that the ordering of these ions was linked to the successive phase transitions. From the X-ray diffraction study [3], the disorder state of the pyridinium and tetrafluoroborate ions was also reported. However, a report of the crystal structure analysis at low temperature was not found. The crystal structure analyses at low temperature phases in PyBF_4 were very important in order to clarify the mechanism of the successive phase transition in this material.

Re-investigation of the single-crystal X-ray structure analysis in

PyBF₄ at room temperature was carried out, and we confirmed that the pyridinium and tetrafluoroborate ions were in the disorder state. Now, we are doing the X-ray structure analyses of low temperature phases in PyBF₄ single-crystal. In congress, we will show the crystal structures of low temperature phases and discuss the successive phase transition mechanism in PyBF₄.

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Keywords: single-crystal X-ray analysis, ferroelectric phase transitions, pyridinium tetrafluoroborate C₅H₆NBF₄

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Magnetism, Ferroelectricity and Lattice Modulation of RMn₂O₅

Yukio Noda^a, Hiroyuki Kimura^a, Youichi Kamada^a, Satoru Kobayashi^b, Kay Kohn^c, Naoshi Ikeda^d, Yusuke Wakabayashi^e, ^a*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan.* ^b*NDE and Science Research Center, Iwate University, Japan.* ^c*Department of Physics, Waseda University, Japan.* ^d*JASRI-SPRING8, Japan.* ^e*PF-IMMS-KEK, Japan.* E-mail: ynoda@tagen.tohoku.ac.jp

A series of rare-earth manganese oxides RMn₂O₅ (R = rare-earth, Y, Bi) shows unique characteristic on magnetism and ferroelectricity. They transform successive phase transitions of antiferromagnetic and incommensurate magnetic ordering accompanied by a dielectric phase transitions. Measurements of the dielectric constant and pyroelectric current revealed that the spontaneous polarization along the *b*-axis appears at the paraelectric (PE)–ferroelectric transition temperature at *T*_{C1} (FE1 phase), followed by anomalies both of the dielectric constant and spontaneous polarization at *T*_{C2} (FE2 phase). Phase transition temperatures of magnetic ordering and dielectric anomalies are completely coincidental.

In order to know the displacement pattern and the origin of the electric-polarization, we have performed synchrotron x-ray diffraction experiments at PF-4C beam line. New satellite reflections were found just at the position of 2 \mathbf{q}_M , where \mathbf{q}_M means the magnetic propagation vector observed by neutron diffractions. Then, FE1 phase is simultaneously commensurate in magnetic and crystal structures, while PE and FE2 phases are incommensurate both in magnetic and crystal structures. We will discuss the possible structure of the ferroelectric phase.

Keywords: phase transitions, ferroelectrics, magnetic ordering

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Crystal Structure, Phase Transitions and Negative Thermal Expansion in the Relaxor Ferroelectric PZN

Erich Kisi, Jennifer Forrester, *School of Engineering, The University of Newcastle, 2308 Australia.* E-mail: Erich.Kisi@newcastle.edu.au

Lead zinc niobate - lead titanate (PZN-*x*PT) single crystals with 0 < *x* < 0.1, show 'giant' piezoelectric strains for electric fields applied along [001] referred to the parent cubic unit cell. However the crystals are reportedly rhombohedral with spontaneous polarization along [111]. This has been accompanied by reports of some interesting structural phenomena including (i) a continuous electric field-induced phase transition from rhombohedral (*R3m*) to monoclinic (*Cm* or *Pm*) symmetry although phase transitions between *R3m* and *Cm* (or *Pm*) must be discontinuous under Landau theory and (ii) pure PZN crystals that are *not* rhombohedral, but rather internally cubic with rhombohedrally distorted exteriors, the so-called X-phase [1].

This paper addresses the baseline structure of PZN which must be properly established before the properties of PZN-*x*PT may be understood. It presents a very high resolution powder neutron diffraction study of the phase transitions in PZN between 4.2 and 450K. The PZN structure is unequivocally rhombohedral in space group *R3m* with *a*=4.06071(7) and α =89.8683(5) at 4.2K. There are no signs of an octahedral tilting transition to *R3c* as is observed in some parallel systems (eg PZT). The transition to the cubic phase occurs

continuously with a critical temperature of ~370K. A previously unknown region of negative thermal expansion occurs over the upper 60K of the rhombohedral phase field.

[1] Xu G., Hiraka H., Shirane G., Ohwada K., *Appl. Phys. Lett.*, 2004, **84**, 3975.

Keywords: ferroelectrics, phase transitions, perovskites

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Rochelle Salt – A Structural Reinvestigation with Improved Tools

Frode Mo^a, Jon A. Beukes^a, Ragnvald H. Mathiesen^b, Khanh M. Vu^a, ^a*Dept. of Physics, NTNU, N-7491 Trondheim.* ^b*SINTEF Materials and Chemistry, N-7465 Trondheim, Norway.* E-mail: fmo@phys.ntnu.no

Rochelle salt (RS), NaKC₄H₄O₆ · 4H₂O is the oldest and was for a long time the only known ferroelectric. It is unusual in that it has two Curie points. RS has been the subject of numerous diffraction and spectroscopy studies over the past 60 years. All published crystallographic indices indicate deficiencies in the data, presumably as a result of the relative instability of the crystals.

Like many other hydrates RS is unstable and deteriorates easily, either by dehydration or liquefaction when exposed to relative humidities (RH) outside the stable range. Dehydration is initiated very quickly and appears to accelerate under exposure to X-rays. Because of this extreme sensitivity to X-rays it is not possible in practice to obtain good diffraction data for RS without conditioning the environment of the crystal and speeding up data collection.

We have developed a gas-flow thermostat sample cell with control of RH, equipped in addition with a transparent rotatable capacitor for the application of an electric DC field in a fixed crystallographic direction on the sample during the experiment [1]. With this cell we were able to collect excellent data both for the high-T paraelectric and the ferroelectric phases using synchrotron radiation. The latter phase undergoes a fast and apparently irreversible transformation under X-radiation. We have also acquired data for this phase. The new data enable a study of these structures with unprecedented precision.

[1] Mo F., Ramsøskar K., 2005, *manuscript in preparation.*

Keywords: ferroelectrics, phase transitions and structure, synchrotron radiation

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Temperature-Composition Phase Diagram of PZN-PT Studied by High Resolution Neutron Powder Diffraction

Jennifer Forrester, Erich Kisi, *School of Engineering, The University of Newcastle, 2308, Australia.* E-mail: jforrest@mail.newcastle.edu.au

Lead zinc niobate – lead titanate (PZN-PT) has exceptional piezoelectric properties. Until five years ago, the pseudo-binary lead zirconate – lead titanate (PZT) and PZN-PT phase diagrams had many features in common. In particular, both had a morphotropic phase boundary between a rhombohedral (*R3m*) and tetragonal (*P4mm*) phase, bounded above by a cubic phase (*Pm3m*). The piezoelectric properties of both are optimal close to the morphotropic phase boundary. More recently, there have been major changes to the PZT phase diagram with the reporting of a large monoclinic (*Cm*) phase field adjacent to the morphotropic boundary and conflicting reports of low temperature modifications to the structures. Whether PZN-PT has similar structural modifications has not been addressed adequately in the literature.

This study presents the results of a very high resolution neutron powder diffraction study of the temperature-composition phase diagram of PZN-PT using the technologically interesting compositions PZN, PZN-4.5%PT and PZN-8%PT. Samples were crushed flux-grown single crystals and were studied at temperature intervals of 5-15K between 4.2 and 450K. Details of the temperature and composition induced phase transitions in PZN-PT will be presented.

Keywords: ferroelectrics, phase transitions, perovskites