$PyBF_4$ 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 $PyBF_4$ single-crystal. In congress, we will show the crystal structures of low temperature phases and discuss the successive phase transition mechanism in $PyBF_4$.

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Keywords: single-crystal X-ray analysis, ferroelectric phase transitions, pyridinium tetrafluoroborate $C_5H_6NBF_4$

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Magnetism, Ferroelectricity and Lattice Modulation of RMn_2O_5

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A series of rare-earth manganese oxides RMn_2O_5 (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

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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 (*R*3*m*) to monoclinic (*Cm* or *Pm*) symmetry although phase transitions between *R*3*m* 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 *R*3*m* with a=4.06071(7) and α=89.8683(5) at 4.2K. There are no signs of an octahedral tilting transition to *R*3*c* 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

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Rochelle salt (RS), $NaKC_4H_4O_6 \cdot 4H_2O$ 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

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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 (*R*3*m*) and tetragonal (*P*4*mm*) phase, bounded above by a cubic phase (*Pm*3*m*). 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