

Observation of Intermediate Phases Between Rhombohedral and Tetragonal PZN-PT by Powder Diffraction.

B. Noheda, D.E. Cox, G. Shirane (BNL, Physics), S-E. Park, L.E. Cross (Penn. State U.), K. Fujishiro (Tech. Inst. Tokyo), Y. Yamada and Y. Uesu (Waseda U.).

Abstract No. nohe7085

Beamline(s): X7A

Solid solutions of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and PbTiO_3 (PZN-PT) are attracting considerable attention due to their remarkable electromechanical properties. They have a cubic perovskite-type structure at high temperatures, but undergo a diffuse ferroelectric phase transition at lower temperatures [1]. Materials in the ferroelectric region were believed to have structures with either rhombohedral or tetragonal symmetry, separated by a "morphotropic" phase boundary (MPB) at $x \approx 10\%$, very similar to that of the well-known piezoelectric system $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) [2]. Extraordinarily high electromechanical couplings and micro-strain levels have been reported by Park and Shrout [3] in rhombohedral crystals that are poled along the $\langle 001 \rangle$ directions, despite the fact that the polar axis lies along [111].

X-ray diffraction experiments performed on rhombohedral PZN-8PT crystals under an applied electric field along [001] have successfully shown that the lattice parameter vs. field loop exactly reflects the strain behavior [4]. The jump observed in the strain vs. field loop at $E = 15$ kV/cm was attributed by these authors to a structural phase transition between the rhombohedral and the tetragonal phases. On the other hand, different work on the same type of samples has shown that the high-field induced phase observed in PZN-8PT is not tetragonal, but monoclinic [5] and that it becomes orthorhombic ($a_m = c_m$) when the field is removed (see also X17B1-X7A abstracts in this volume). In order to clarify the structure of these technologically important materials, powder diffraction has been done.

Crystals with compositions 91% $(\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ -9% (PbTiO_3) , 92% $(\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ -8% (PbTiO_3) and 96.5% $(\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3)$ -4.5% (PbTiO_3) (PZN-9PT, PZN-8PT and PZN-4.5PT, respectively) were grown using the high temperature flux technique, as described in Ref. [3]. The crystals were cut into $2 \times 2 \times 2$ mm³ cubes with their faces perpendicular to the $\langle 100 \rangle$ directions. They were either poled ($E \approx 10$ kV/cm) to induce long-range order in the relaxor materials, or exposed to high electric fields ($E > 15$ kV/cm) in order to study the induced phase. A small piece from each of the crystals was then chipped, carefully crushed, meshed and sieved to get grain sizes in the 30-40 μm . Thin capillaries of 0.2 mm diameter were filled with this powder for the diffraction measurements. Powder x-ray diffraction measurements of the rotating capillaries were done at X7A with a wavelength of about 0.7 \AA , using a Si(111) double-crystal monochromator and a Ge(220) analyzer crystal.

Figure 1 shows selected diffraction peaks for PZN-9PT and PZN-4.5PT, after high-field exposure and poling, respectively. The profiles corresponding to PZN-9PT clearly show a monoclinic distortion with $a_m = c_m$ (orthorhombic symmetry) after the high electric field is removed, in agreement with the single crystal diffraction investigations in PZN-8PT [5]. On the other hand, the profiles corresponding to a PZN-4.5PT composition, which is further away from the MPB, show neat rhombohedral distortion after poling. Work is in progress to characterize the effect of the electric field in these materials, at both sides of the MPB, by means of both single-crystal and powder x-ray diffraction.

Acknowledgments: This work has been supported by the U.S.DOE contract No. DE-AC02-98CH10886.

References: [1] J. Kuwata *et al.*, *Japan. J. of Applied Phys.* **21**, p.1298 (1982). [2] B. Jaffe *et al.*, "Piezoelectric Ceramics", Academic Press, London (1971). [3] S-E. Park and T.R. Shrout, *J. Appl. Phys.*, **82**, p. 1804 (1997). [4] M.K. Durbin *et al.* *Appl. Phys. Lett.* **74**, p. 2848 (1999); *J. Appl. Phys.*, **87**, p. 8159 (2000). [5] B. Noheda *et al.* submitted (e-print: cond-mat/0009227).

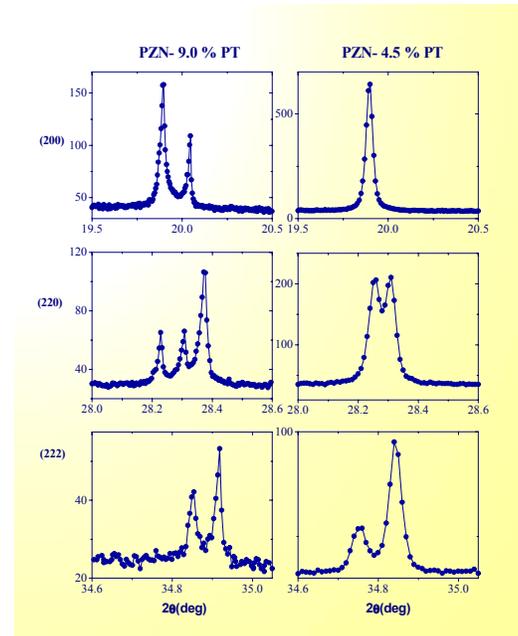


Figure 1. Selected peaks from the powder diffraction profiles of PZN-9PT (left) and PZN-4.5PT (right).