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.

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