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THE CHARACTERIZATION OF HIGH TEMPERATURE SOLUTION-GROWN SINGLE CRYSTALS OF $Pb(Fe_{1/2}Nb_{1/2})O_3$

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Abstract - Polarization microscope studies on single crystal samples of $Pb(Fe_{1/2}Nb_{1/2})O_3$ [PFN] have been made. Thin platelets (<60μ) show large, homogeneous ferroelectric domains and optical characterization shows PFN is trigonal at room temperature and optically negative. Birefringence measurements between 4.2K and 400K reveal the transition to the cubic structure takes place at 383K, in accordance with earlier work, but they also locate a previously undetected structural modification at 354K, accompanied simultaneously by a re-orientation of the index ellipsoid; both transitions manifest themselves by endothermic reactions on heating in DTA experiments. The new phase is very likely monoclinic.

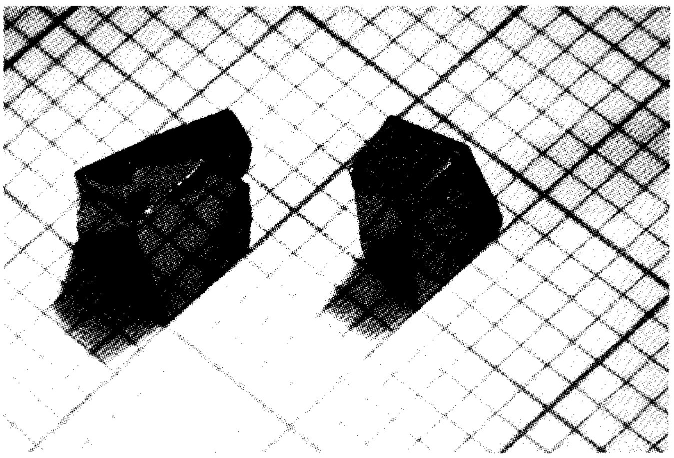
INTRODUCTION

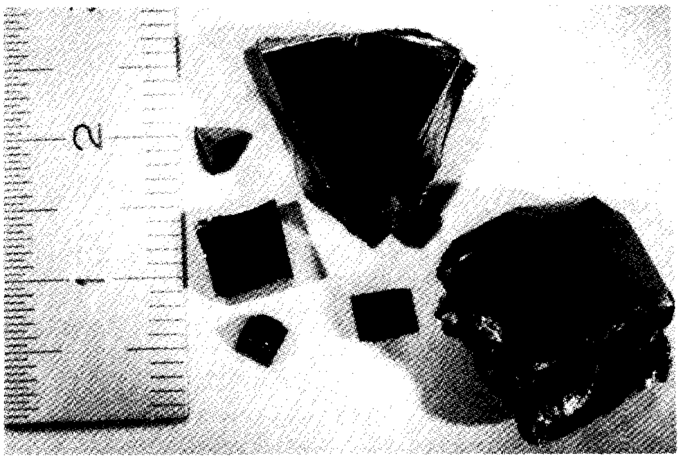
For over two decades the perovskite $Pb(Fe_{1/2}Nb_{1/2})O_3$ [PFN] has been the subject of a number of studies, which report it as a trigonal ferroelectric below 383K[1]. Above this temperature it is cubic, whereas, at lower temperatures, magnetic ordering has been observed. The antiferromagnetic Néel point, T_N, has been located at 9K[2], although the same authors recorded anomalies in the magnetic susceptibility above this temperature, in the region of 125K and 65K. In addition, they measured a weak ferromagnetic moment when electric and magnetic fields were applied to the crystal. A recent investigation[3] on a ceramic found a T_N at 155K and no indication of a transition below this temperature. The role of the reportedly random distribution of Fe^{3+} and Nb^{5+} ions in differently prepared samples may partly account for this discrepancy.

Most of the earlier work has been on ceramic samples or on small single crystals (≦0.8mm cube)[2] and, as a result, optically-controlled domain studies have never been attempted. Very often the use of a polarization microscope can help to clarify non-optical measurements or may even reveal new phenomena and it was with this objective in mind that the present project was conceived. A pre-requisite is, naturally, a supply of good quality single crystals of suitable dimension and their growth from high temperature solution is reported elsewhere[4]. In this paper we report on preliminary room temperature investigations of PFN with the polarization microscope and subsequent measurement of the optical anisotropy between 4.2K and the cubic phase. Above room temperature, differential thermal analysis (DTA) has helped complement the results of the optical investigations.

EXPERIMENTAL

Some of the as-grown PFN crystals showed well-formed pseudo-cubic facets and were typically of the order of 3-4 mm.cube edge with several measuring over 10 mm (but these exhibited rounded, less regular facets). Several are shown in Figures 1 and 2. They were very dark red, nearly black, and showed a high degree of lustre, illustrating a high index of refraction. It was possible to observe ferroelectric domains on natural





FIGURES 1 and 2 PFN crystals grown from high temperature solution. Temperature stability (∿0.1deg) and a slow cooling rate (∿0.4deg h^{-1}) were some of the factors responsible for the good quality samples.

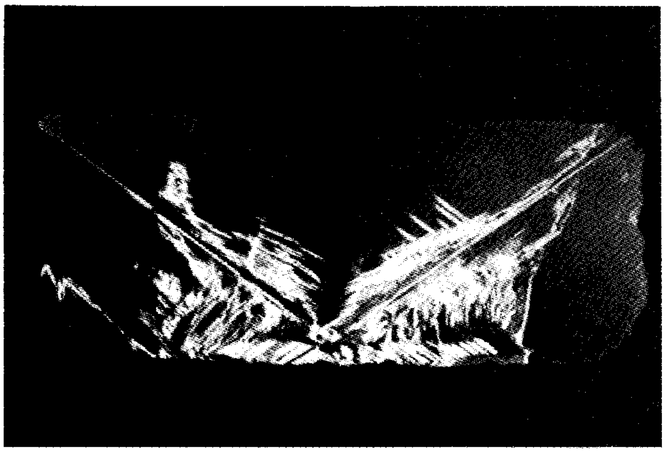
surfaces in reflected light with nearly crossed polars but for transmission studies it was necessary to cut and polish platelets of about 60µm thickness whereupon they were striking red in colour. Observations were made along the cubic <100>, <110>, and <111>-type directions.

A Leitz Orthoplan microscope was available with camera and photomultiplier (EMI S20/9558B) accessories. Birefringence was measured with Leitz tilting compensators M (upto 4 orders) and K (upto 10 orders) in conjunction with a Leitz heating stage 1350 between 290K and 400K and a modified Oxford Instruments CF204 helium exchange gas continuous flow cryostat for lower temperatures. DTA studies were performed in static air with a Mettler TA2000 apparatus, using an Al_2O_3 reference with a heating rate of 4 deg min^{-1}.

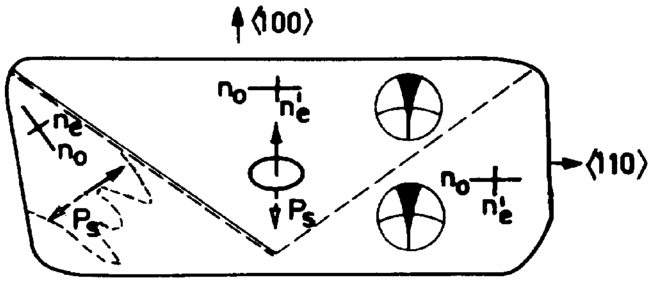
RESULTS

Room temperature observations revealed, in general, large ferroelectric domains which showed good homogeneity and sharp extinction in agreement with a trigonal symmetry. Two examples are found in Figures 3 and 4 with accompanying schematics indicating the orientation of the optical indicatrices and conoscopic figures. (Several samples were entirely monodomain). Strain birefringence in the domains with the c-axis perpendicular to the (111) platelet was very often of the order of 4×10^{-5} (determined with a photoelastic modulator[5]) and, under conoscopic illumination, this gave rise to an opening of the uniaxial optic-axis interference figure, a cross, upon sample rotation. This effect was very much smaller if there was less strain ($\sim 10^{-5}$) present in the domain, as we see when the two cases are compared in Figure 5. The optic sign of PFN at room temperature is negative.

The birefringence of PFN is rather large, 76×10^{-3}, at room temperature and reaching 117×10^{-3} at 4.2K; it is displayed in Fig. 6. The platelets become optically isotropic at 383K but this transition is preceded by a sharp change in Δn at 354K, accompanied by a rotation of the index ellipsoid to a direction aligned along the $<110>_{cub}$-type axes (see Fig.7). The measurement shown here was taken on the principal section of the (110) sample in Figure 3. Similar data was gathered for the other major crystallographic directions to positively verify this conclusion. The new geometry of the ellipsoid suggests we have a monoclinic phase in the region 354K and 383K, although the onset of a slight rotation as early as ∿335K probably results from a slight strain in the crystal.

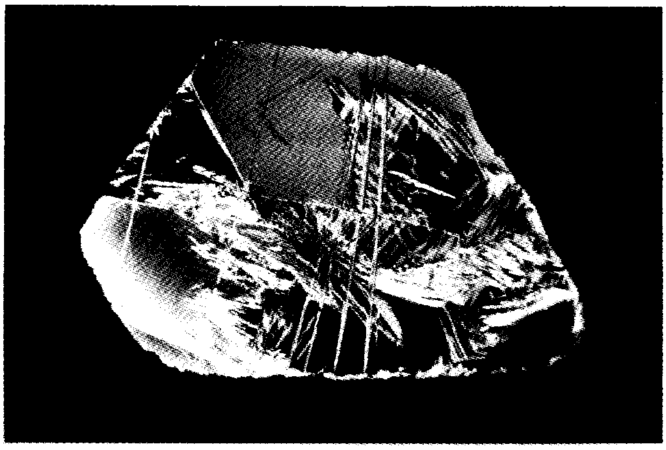


(a)

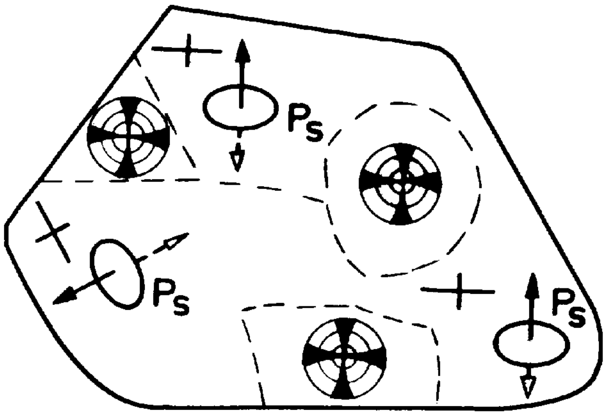


(b)

FIGURE 3 A PFN $(110)_{cub}$ platelet (a) of 40µm thickness, with an accompanying schematic (b), indicating the extinction and optic axis directions in the ferroelectric domains.



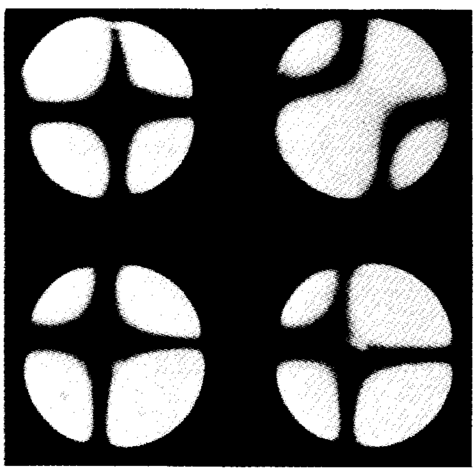
(a)



(b)

FIGURE 4 A $(111)_{cub}$ section (a), with the c-axis perpendicular to three of the domains (extinct), shown by the schematic (b)

I $I^{45°}$



II $II^{45°}$

FIGURE 5 Conoscopic figures for two ferroelectric domains with the c-axis mutually perpendicular. Domain I shows higher strain birefringence than II and so the cross opens more upon rotation by 45°

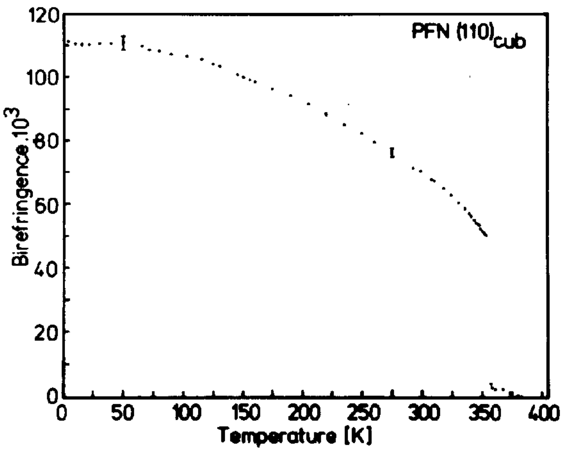


FIGURE 6 The temperature dependence of the principle birefringence measured on a 40µm $(110)_{cub}$ platelet (with a tilting compensator) (λ= 546nm).

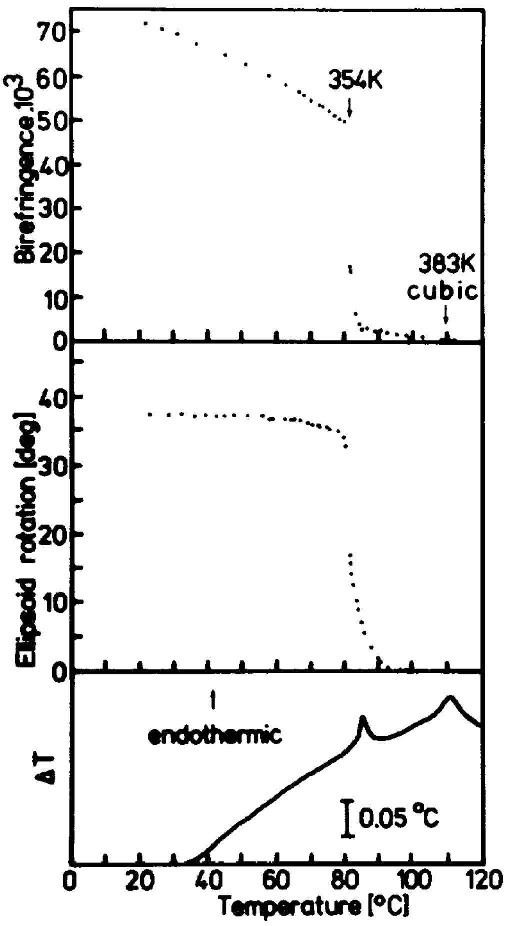


FIGURE 7 Birefringence and DTA measurements reveal two transitions, at 354K and 383K. The former is accompanied by a rotation of the optical indicatrix.

The birefringence did not reveal any crystallographic change between 4.2K and 354K but a closer study with the more sensitive photoelastic modulator technique is planned.

The DTA measurement in Fig.7 was made on an as-grown single crystal and both transitions are clearly demonstrated by endothermic peaks, corresponding to enthalpy changes, ΔH of $\sim 0.04\ Jg^{-1}$(354K) and 0.07 Jg^{-1}. The specific heat, C_p, at 354K was estimated at 0.37 $JK^{-1}g^{-1}$. These values are at variance with the ceramic work of Bhat et al.[6] who observed only the 383K transition and a larger ΔH and smaller C_p.

It is not yet understood why previous workers have not observed the transition at 354K, although a possible explanation may lie in the degree of ordering present between Fe^{3+} and Nb^{5+}. X-ray procession studies[7] at room temperature on our crystals do not indicate any ordering, in agreement with the conclusions of earlier publications. However, Raman scattering may prove more sensitive in this respect and is foreseen for the near future, as are magnetic susceptibility and dielectric constant measurement on single domains.

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