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LETTER TO THE EDITOR

Ferroelectricity in disordered $Pb(In_{1/2}Nb_{1/2})O_3$

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Abstract. Polarisation–electric field (P–E) hysteresis loops in disordered lead indium niobate ($Pb(In_{1/2}Nb_{1/2})O_3$; PIN) are, for the first time, observed. The value of the spontaneous polarisation P_s is 10.8 $\mu C\ cm^{-2}$ at −20 °C and decreases rapidly near −5 °C. Therefore, the ferroelectricity in disordered PIN has been confirmed. Moreover, a new dielectric anomaly is found at a temperature T_t of 116 °C. This temperature T_t is thought to correspond to the previously reported phase transition temperature at 95 °C found using an x-ray diffraction technique. Above this phase transition temperature, the dielectric dispersion observed at temperatures below T_t disappears and the permittivity obeys the Curie–Weiss law. Such dielectric behaviour in disordered PIN is strikingly different from that in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ family with the diffuse phase transition characterised by the strong dielectric dispersion.

Perovskite compounds have been of fundamental and practical interest for many years (Lines and Glass 1977). It has been reported that some perovskite compounds of the $Pb(B_{1/2}Nb_{1/2})O_3$ (B = Cr, Fe, Mn, Sc, In, Lu, Yb, Tm) series are ferroelectrics and some (B = Lu, Yb, Tm) are antiferroelectrics (Fesenko 1972). The changeover from ferroelectric to antiferroelectric behaviour has been pointed out to be at the ionic radius possessed by In and Sc (Fesenko 1972, Prokopalo *et al* 1982, Kupriyanov *et al* 1983, Groves 1986a, b). Much attention has been given to the phase transition of lead indium niobate ($Pb(In_{1/2}Nb_{1/2})O_3$; PIN) (Turik *et al* 1980, 1985, Prokopalo *et al* 1982, Bokov *et al* 1983, 1986, Kupriyanov *et al* 1983, 1984, Groves 1985, 1986a, b). Recent work shows that PIN lies very close to the boundary between order and disorder in the cation (In^{+3},Nb^{+5}) arrangement on the B sites in a perovskite structure (Prokopalo *et al* 1982, Bokov *et al* 1983, 1986, Kupriyanov *et al* 1984, Turik *et al* 1985). The degree of compositional ordering of the B sites of the perovskite structure has been thought to vary with the fabrication process (Feng and Schulze 1988) and heat treatment (Setter and Cross 1980, Stenger and Burgraaf 1980). It is known that PIN specimens prepared by the usual mixed oxide method, starting with oxides PbO, In_2O_3 and Nb_2O_5, can be obtained in a disordered state (Turik *et al* 1980, Prokopalo *et al* 1982, Kupriyanov *et al* 1983), and can be made to exhibit a transition from disorder to order by suitable heat treatment (Prokopalo *et al* 1982, Bokov *et al* 1983, 1986, Kupriyanov *et al* 1984, Turik *et al* 1985). Disordered PIN has been known to exhibit a diffuse phase transition (DPT) characterised by strong dielectric dispersion (Turik *et al* 1980, Kupriyanov *et al* 1983, Groves 1985) as observed in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) (Smolensky 1970, Kirillov and Isupov 1973, Schmidt *et al* 1981). It has been suggested that disordered PIN is ferroelectric (Turik *et al* 1980, Kupriyanov *et al* 1983) and ordered PIN is antiferroelectric (Prokopalo

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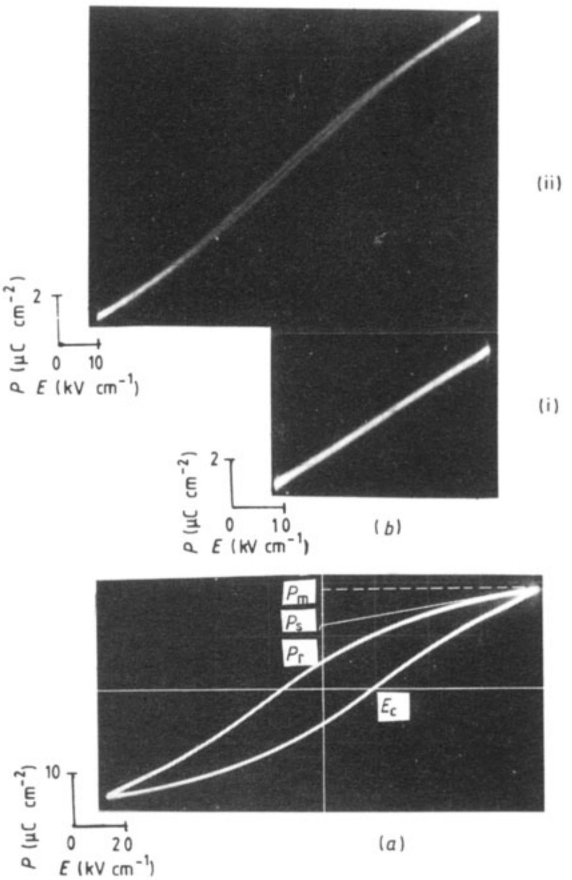

Figure 1. (*a*) The *P–E* hysteresis loop at −20 °C with the 60 Hz AC electric field amplitude at 78 kV cm^{-1}, and (*b*) the *P–E* relation at 80 °C with the AC amplitude of (i) 20 kV cm^{-1} and (ii) 50 kV cm^{-1} of disordered PIN.

et al 1982, Kupriyanov *et al* 1984, Turik *et al* 1985). However, ferroelectricity in disordered PIN or antiferroelectricity in ordered PIN has not been confirmed by observation of polarisation–electric field (*P–E*) hysteresis, or of double hysteresis loops. Moreover, for PIN single crystals prepared by the PbO–B_2O_3 flux method, the *P–E* relation was reported to be elliptical (Turik *et al* 1980, Bokov *et al* 1983, Kupriyanov *et al* 1983). The reason for this may be related to the effect of the introduction of impurity ions into crystals from the flux. In this work, pure PIN ceramics with perovskite single phase are prepared through the formation of the wolframite phase oxide ($InNbO_4$) and are obtained in a disordered state. The *P–E* hysteresis loop is, for the first time, observed in disordered PIN (see figure 1), and thus the ferroelectricity is confirmed. Moreover, a new dielectric anomaly is found at a temperature T_t of 116 °C, corresponding to the phase transition temperature determined previously by the x-ray diffraction method (Turik *et al* 1980, Kupriyanov *et al* 1983). At temperatures above T_t, the dielectric dispersion observed at temperatures below T_t disappears and the permittivity obeys the Curie–Weiss law. Such dielectric characteristics are qualitatively different from those in

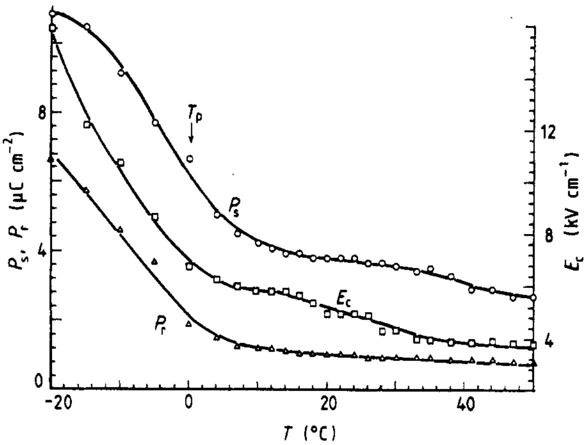

Figure 2. Dependence on temperature, T, of the spontaneous polarisation P_s, the remanent polarisation P_r and the coercive field E_c of disordered PIN.

the PMN family with the DPT (Smolensky 1970, Kirillov and Isopov 1973, Schmidt *et al* 1981). Also in this letter, we report the temperature dependence of dielectric properties of disordered PIN such as the spontaneous polarisation and the permittivity, and clarify the difference in dielectric properties between disordered PIN and the PMN family with the DPT.

PIN specimens were prepared through the formation process of prereacting indium and niobium oxides to form the wolframite phase oxide ($InNbO_4$) prior to reaction with PbO by the fabrication technique developed by Swartz and co-workers (Swartz and Shrout 1982, Yasuda and Shibuya 1989). X-ray powder patterns of ceramic specimens showed rhombohedral patterns (a = 4.119 Å, and α = 89.96°) at room temperature as reported previously (Turik *et al* 1980, Kupriyanov *et al* 1983). Evidence of superstructure from ordering of In and Nb was not found. X-ray diffraction confirms that the specimen is single-phase. The apparent density of the ceramics was 92% of the theoretical density. The specimen (of thickness 0.15 mm and diameter 4 mm) was electroded with silver paste (Dupont No 7075) by firing at 590 °C for 5 min. The electrical capacitance was measured at 1, 10 and 100 kHz with a field weaker than 10 V cm^{-1} using an *LCR* meter and the spontaneous polarisation was examined with a Sawyer–Tower circuit. All the dielectric data were collected while increasing temperature at a rate of 0.2 K min^{-1}. These results were found to be reproducible from sample to sample.

P–E hysteresis loops at 60 Hz of disordered PIN for different temperatures are shown in figure 1. The maximum polarisation P_m first increases rapidly, and then gradually, with increasing applied elastic field strength. The *P–E* hysteresis loop is in the form of a rounded curve. As the temperature increases, the *P–E* hysteresis loop becomes narrow and the remanent polarisation P_r very small. For example, at 80 °C, with increasing electric field strength, the relation between P and E is at first linear, for electric fields up to about 20 kV cm^{-1}, and then becomes slightly non-linear as shown in figure 1(*b*). The temperature dependences of the spontaneous polarisation P_s, the remanent polarisation P_r and the coercive field E_c obtained from *P–E* hysteresis loops are shown in figure 2. The value of P_s is estimated to be 10.8 μC cm^{-2} at -20 °C. With increasing temperature T, the value of P_s decreases rapidly between -20 °C and 0 °C, and above a temperature

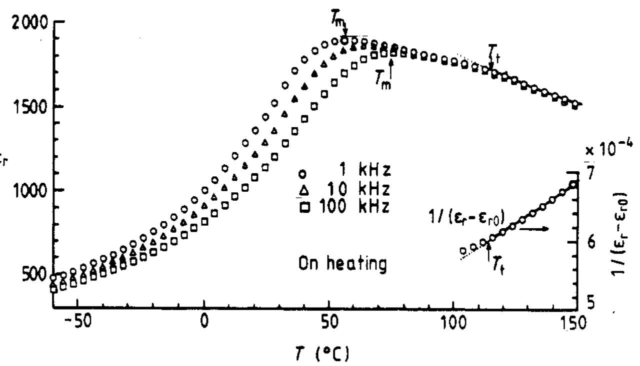

Figure 3. Dependence on temperature, T, of the relative permittivity ε_r (and its inverse) of disordered PIN measured at 1, 10 and 100 Hz with a field weaker than 10 V cm^{-1}. The full curve shows the values of ε_r calculated from equation (1).

T_p of 0 °C, the rate of decrease of P_s with temperature becomes very slow. No dielectric anomaly near T_p on the permittivity versus T curve corresponding to this rapid decrease in P_s with T is seen (see figure 3). Such dielectric behaviour was also observed in PMN with the DPT (Smolensky 1970, Schmidt *et al* 1981, Smolensky *et al* 1981). The temperature dependence of the remanent polarisation P_r and the coercive field E_c is similar to that of P_s. At higher temperatures, P–E hysteresis loops give erroneous values for P_s because of their non-linearities (Lines and Glass 1977) as seen in figure 1(*b*).

The temperature dependence of the relative permittivity ε_r of disordered PIN for different frequencies is shown in figure 3. The value of ε_r shows a broad maximum at a temperature T_m, which is shifted towards higher temperatures with increasing frequency (T_m: 56 and 76 °C at 1 and 100 kHz, respectively). Such behaviour of ε_r is in agreement with the dielectric dispersion reported previously for disordered PIN (Turik *et al* 1980, Kupriyanov *et al* 1983, Groves 1985). Moreover, ε_r shows a new dielectric anomaly at a temperature T_t of 116 °C—seen as an inflection point on the ε_r versus T curve in figure 3. It is thought that this temperature T_t corresponds to the phase transition temperature at 95 °C found from an abrupt change of the cell parameter by the x-ray diffraction method (Turik *et al* 1980, Kupriyanov *et al* 1983). The lower value of the phase transition temperature, reported to be 95 °C, may be related to the effect of impurity ions introduced into crystals from the flux on the phase transition (Clarke and Whatmore 1976) as the PIN crystals used in the x-ray diffraction method were prepared by the flux method (Turik *et al* 1980, Kupriyanov *et al* 1983). At temperatures above T_t, the dielectric dispersion disappears and ε_r obeys the Curie–Weiss law (see $1/(\varepsilon_r - \varepsilon_{r0})$ in figure 3)

$$\varepsilon_r = \varepsilon_{r0} + C/(T - T_0) \tag{1}$$

where the Curie constant C is 4.3×10^5 K, the Curie–Weiss temperature T_0 is -148 °C and the constant ε_{r0} is 46. These values of both C and the difference $T_t - T_0 = 264$ K obtained for disordered PIN are compared with those ($C = 2.2 \times 10^5$ K and $T_t - T_0 = 220$ K) reported for ordered PIN, which has been suggested to be antiferroelectric (Prokopalo *et al* 1982, Bokov *et al* 1983, Turik *et al* 1985). The rapid decrease in P_s with temperature between -20 °C and 0 °C, far below T_m, and the dielectric dispersion around T_m seen in figures 2 and 3 have also been reported for PMN with the DPT (Smolensky 1970, Schmidt *et al* 1981, Smolensky *et al* 1981). Such a dielectric dispersion has been explained in terms of the relaxation model of the isolated polar regions, i.e. the regions of spontaneous polarisation surrounded by a non-polar phase (Smolensky 1970, Kirillov and Isupov 1973). Despite these similarities, such dielectric behaviour as the dielectric anomaly at T_t, the disappearance of the dielectric dispersion and the temperature dependence of ε_r represented by the Curie–Weiss law (equation (1)) above T_t sets disordered PIN apart from the PMN family with the DPT (Smolensky 1970, Schmidt *et al* 1981, Smolensky *et al* 1981). Although the PIN specimens prepared by the usual mixed oxide method starting with oxides PbO, In_2O_3 and Nb_2O_5 have been reported to exhibit a transition from disorder to order on annealing at 650 °C for an hour (Prokopalo *et al* 1982, Turik *et al* 1985), the variation of the degree of compositional ordering in the cation (In^{+3}, Nb^{+5}) arrangement on the B sites of disordered PIN prepared through the formation of the wolframite phase oxide ($InNbO_4$) for this study has, up to now, not been observed, even on annealing at 650 °C for 60 hours. Further experiments on PIN, involving dielectric measurements under pressure, are now in progress.

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