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## Temperature and pressure dependence of dielectric properties of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ with the diffuse phase transition

Naohiko Yasuda and Yoshitaka Ueda

Department of Electrical Engineering, Gifu University, Gifu, 501-11, Japan

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**Abstract.** The temperature  $T$  (30–150 °C) and pressure  $p$  (0–6 kbar) dependence of the dielectric properties (relative permittivity  $\epsilon_r$ , dielectric loss tangent and spontaneous polarisation) of ferroelectric  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics synthesised by the use of alkoxides are presented. The relative permittivity  $\epsilon_r$  has a broad maximum at the ferroelectric transition temperature  $T_i$ . The results also showed that at  $T > T_i$ ,  $(1/\epsilon_r - 1/\epsilon_{r,\text{max}})$  is proportional to  $(T - T_i)^\gamma$ , where  $\epsilon_{r,\text{max}}$  is the peak value of  $\epsilon_r$  at  $T_i$  and  $\gamma$  is a constant. The value of the exponent  $\gamma$  was found to be equal to 2.0 and remained almost independent of the applied pressure. With increasing pressure,  $p$ , the values of both  $T_i$  and  $\epsilon_{r,\text{max}}$  were reduced. In the case of  $T_i$  the reduction was linear with  $dT_i/dp = -3.7 \text{ K kbar}^{-1}$ . With increasing DC bias fields  $E_d$ , the maximum value of  $\epsilon$  is lowered, the shape of its curve becomes more rounded and  $T_i$  is displaced towards higher temperatures with  $dT_i/dE_d = 0.7 \text{ K cm kV}^{-1}$ . The temperature and pressure dependence of the permittivity and the spontaneous polarisation is explained in terms of a phenomenological theory.

### 1. Introduction

Much attention has been given to diffuse phase transitions (DPT) from the points of view of fundamental interest and of practical importance in the development of ferroelectric materials for, e.g., capacitor applications (Smolensky 1970, 1984, Shrout and Halliyal 1987). Complex perovskite-type ferroelectric materials with disordered cation arrangements show DPT characterised by a broad maximum for the temperature dependence of the permittivity and the dielectric dispersion in the transition region (Smolensky 1970, 1984).  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) is a ferroelectric of the disordered type (Smolensky *et al* 1958, Bokov *et al* 1962), having a ferroelectric transition temperature at 110 °C at atmospheric pressure (Smolensky *et al* 1958, Isupov *et al* 1960, Bokov *et al* 1962, Bhat *et al* 1974, Brunskill *et al* 1981). However, it is interesting to note that PFN does not show a frequency dispersion of the dielectric maximum in the frequency range from 100 Hz to 4.5 MHz (Isupov *et al* 1960, Shrout *et al* 1984). On the other hand, PFN was reported to have low resistivity (of order  $10^8 \Omega \text{ cm}$  at room temperature) (Isupov *et al* 1960). Little has been reported on the temperature and pressure dependence of the spontaneous polarisation  $P_s$  of PFN. In this work, the breakdown electric field strength was increased by the synthesis of PFN via alkoxides, making it possible to observe well-saturated polarisation  $p$ -electric field hysteresis loops (Yasuda and Ueda 1988). The value of

$P_s$  ( $13.5 \mu\text{C cm}^{-2}$  at  $-136^\circ\text{C}$  at atmospheric pressure) of PFN ceramics prepared for this study is much larger than that ( $6.2 \mu\text{C cm}^{-2}$ ) reported previously (Isupov *et al* 1960). The temperature dependence of  $P_s$  and the strongly broadened permittivity versus temperature curve for PFN was also reported (Yasuda and Ueda 1988). In this paper, the temperature and pressure dependence of the dielectric properties such as the permittivity and the spontaneous polarisation of PFN ceramics prepared via alkoxides are presented and explained in terms of a phenomenological theory.

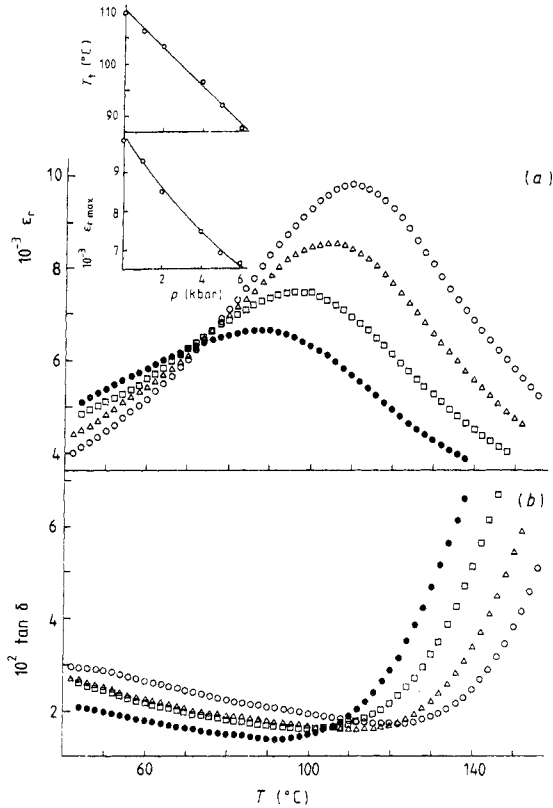
## 2. Experimental methods

PFN ceramics were prepared via alkoxides. Aqueous benzene solution was added dropwise into a mixed benzene solution of iron-butoxide (reagent grade) and niobium-ethoxide (reagent grade) and the resultant precipitate was fired at  $1000^\circ\text{C}$  in air for 1 h to form a wolframite phase oxide  $(\text{FeNb})\text{O}_4$ . The oxide was mixed with PbO powder (purity 99.99%, particle size  $<1 \mu\text{m}$ ) and the intimate mixture was ball-milled with acetone for a day, then dried and pressed into a disc. The discs were calcinated at  $850^\circ\text{C}$  for 3 h, and sintered at  $900^\circ\text{C}$  for 2 h in a controlled PbO atmosphere in a Pt crucible in order to prevent loss of PbO. X-ray powder patterns of ceramic specimens showed rhombohedral patterns (lattice parameters  $a = 4.017 \text{ \AA}$  and  $\alpha = 89.57^\circ$ ) at room temperature as reported previously (Isupov *et al* 1960, Bhat *et al* 1974). Grain sizes were in the range  $1\text{--}1.5 \mu\text{m}$ . The apparent density of the ceramics was 92–95% of the theoretical density ( $8.46 \text{ g cm}^{-3}$ ). X-ray diffraction measurements confirm that the specimen is a single phase. The specimen (of thickness 0.15 mm and diameter 5 mm) was electroded with silver paste (Dupont No. 7075) by firing at  $590^\circ\text{C}$  for 5 min. The electrical capacitance and the dielectric loss tangent were measured at 1, 10 and 100 kHz with a field weaker than  $10 \text{ V cm}^{-1}$  using an AC bridge, and the spontaneous polarisation was examined with a Sawyer–Tower circuit. A pressure device with silicone oil (KF96L-1cs) as a pressure-transmitting fluid was used to apply hydrostatic pressure to the specimen. A detailed description of the high pressure apparatus has been given elsewhere (Yasuda *et al* 1986). All the dielectric data were collected, with good reproducibility, while increasing temperature at a rate of  $0.5 \text{ K min}^{-1}$  at various constant pressures, and all of the data observed were reversible when the pressure was lowered.

## 3. Experimental results and discussion

### 3.1. Relative permittivity and dielectric loss tangent

Figures 1(a) and 1(b) show the temperature dependence of the relative permittivity  $\epsilon_r$  and the dielectric loss tangent  $\tan \delta$  of  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  at 100 kHz for different pressures. The value of  $\epsilon_r$  shows a broad maximum at a temperature  $T_m$  (corresponding to the ferroelectric transition temperature  $T_t$ ), which is independent of frequencies from 1 to 100 kHz. The value of  $T_t$  at atmospheric pressure ( $110^\circ\text{C}$ ) is in agreement with that reported previously (Smolensky *et al* 1958, Isupov *et al* 1960, Bokov *et al* 1962, Brunskill *et al* 1981). As pressure is increased, the maximum in  $\epsilon_r$  shifts towards lower temperatures and becomes broader. The value of  $\epsilon_r$  at  $T < T_t$  increases more slowly with temperature at higher pressures. With increasing pressure, the transition temperature  $T_t$  decreases with a pressure coefficient  $dT_t/dp = -3.7 \text{ K kbar}^{-1}$  and the maximum value of  $\epsilon_r$  ( $\epsilon_{r,\text{max}}$ )



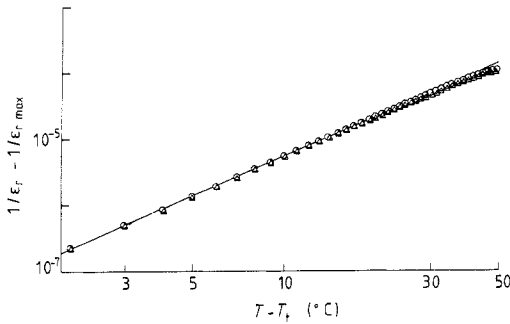
**Figure 1.** The temperature dependence of (a) the relative permittivity  $\epsilon_r$  and (b) the dielectric loss tangent  $\tan \delta$  for different pressures.  $\circ$ , 0 kbar;  $\triangle$ , 2 kbar;  $\square$ , 4 kbar;  $\bullet$ , 6 kbar. Inset: the pressure dependence of the ferroelectric transition temperature  $T_f$  and the maximum value of  $\epsilon_r$  ( $\epsilon_{rmax}$ ).

decreases as shown in the inset in figure 1(a). The dielectric loss peak associated with the dielectric maximum as observed in  $Pb(Mg_{1/3}Nb_{2/3})O_3$  (PMN) with the DPT (Smolensky *et al* 1960) is absent in figure 1(b). With increasing pressure, the  $\tan \delta$  versus  $T$  curve shifts towards lower temperatures along the  $T$  axis and the value of  $\tan \delta$  is reduced in the lower temperature range ( $T \leq T_f$ ). The relative permittivity of ferroelectrics with the DPT deviates largely from the Curie–Weiss law at  $T > T_f$ . Empirically, the relative permittivity  $\epsilon_r$  at  $T > T_f$  has been known to be described by the following relation (Clarke and Burfoot 1974, Uchino and Nomura 1982):

$$1/\epsilon_r - 1/\epsilon_{rmax} = (T - T_f)^\gamma / C' \tag{1}$$

where  $C'$  is the Curie-type constant and  $\gamma$  is an exponent.

Figure 2 shows logarithmic plots of the reciprocal relative permittivity ( $1/\epsilon_r - 1/\epsilon_{rmax}$ ) at 100 kHz against the reduced temperature ( $T - T_f$ ) at 0 and 6 kbar. It is found from the linearity of the curve in figure 2 that equation (1) holds for different pressures. The value of  $\gamma$  is determined to be 2.0 from the slope of the straight line in the temperature range  $2 < (T - T_f) < 42$ . The effect of pressure on the slope of the straight line is hardly observable. This value of  $\gamma$  is almost independent of pressure. The Curie-type constant  $C'$  is estimated from equation (1) to be  $1.7 \times 10^7$  at 0 kbar. Smolensky (1970) has derived a quadratic relation ( $\gamma = 2$ ) on the basis of a microscopic composition fluctuation model.



**Figure 2.** Logarithmic plots of the reciprocal relative permittivity ( $1/\epsilon_r - 1/\epsilon_{r,\max}$ ) at 100 kHz against the reduced temperature ( $T - T_i$ ) for different pressures.  $\Delta$ , 0 kbar;  $\circ$ , 6 kbar.

According to this model (Smolensky 1970, Kirillov and Isupov 1973), the distribution of the local Curie temperature  $\theta$  of microvolume regions is of a Gaussian type;

$$f(\theta) \propto \exp[-(\theta - T_i)^2/2\sigma^2]$$

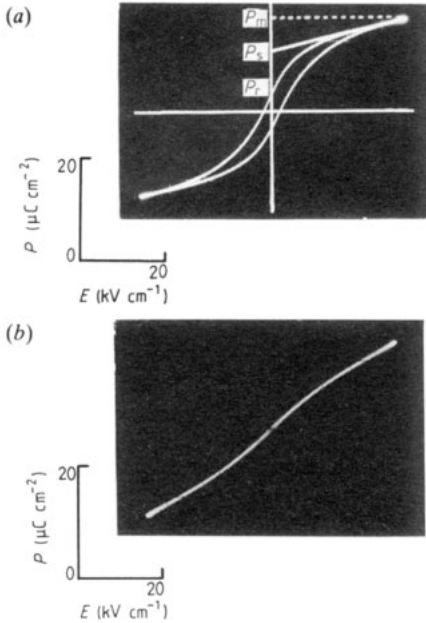
where  $\sigma$  is the standard deviation. The reciprocal relative permittivity can be written in the form (Kirillov and Isupov 1973);

$$1/\epsilon_r = 1/\epsilon_{r,\max} + (T - T_i)^2/2\epsilon_{r,\max}\sigma^2. \quad (2)$$

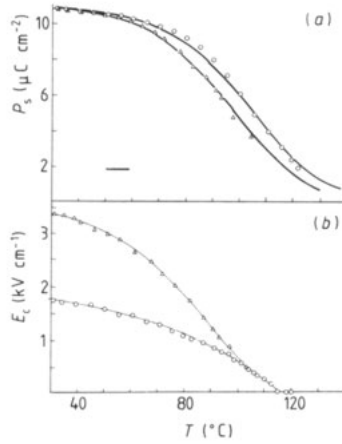
From the curve in figure 2, with the aid of equation (2), the value of  $\sigma$  describing the intensity of the DPT is estimated to be 28 K. At higher temperatures ( $T - T_i > 42$ ), the temperature dependence of the relative permittivity approaches the Curie-Weiss law ( $\gamma = 1$ ), as observed at higher temperatures for PMN (Uchino *et al* 1980).

### 3.2. Spontaneous polarisation

Polarisation–electric field ( $P$ – $E$ ) hysteresis loops, with an AC amplitude of 30 kV cm<sup>-1</sup> and 60 Hz, of PFN for different temperatures at atmospheric pressure are shown in figure 3. The maximum polarisation  $P_m$  first increases rapidly, and then gradually with increasing applied field strength. The  $P$ – $E$  hysteresis loop is in the form of a rounded curve. The value of the spontaneous polarisation  $P_s$  (11.0  $\mu\text{C cm}^{-2}$  at 30 °C) is comparable to that (12–40  $\mu\text{C cm}^{-2}$  at room temperature) estimated from the atomic structure of PFN by microelectron and x-ray diffraction analysis (Platonov *et al* 1970). With increasing temperature, the  $P$ – $E$  hysteresis loop becomes narrow and the remanent polarisation  $P_r$  very small. Figures 4(a) and 4(b) show the temperature dependence of the spontaneous polarisation  $P_s$  and the coercive field  $E_c$  obtained from  $P$ – $E$  hysteresis loops at 0 and 2 kbar, respectively. With increasing temperature, the value of  $P_s$  decreases first gradually, and then rapidly near  $T_i$ . With increasing pressure, the  $P_s$  versus  $T$  curve shifts towards lower temperatures along the  $T$  axis. The major part of the change of  $P_s$  with pressure at constant temperature is caused by the shift of  $T_i$  with pressure. With increasing temperature, the value of  $E_c$  also decreases gradually and then rapidly near  $T_i$ . The value of  $E_c$  increases rapidly with increasing pressure. Note that the



**Figure 3.** Polarisation–electric field ( $P$ – $E$ ) hysteresis loops at atmospheric pressure. (a) At 32 °C, (b) at 115 °C.



**Figure 4.** The temperature dependence of (a) the spontaneous polarisation  $P_s$  (—, calculated values), and (b) the coercive field  $E_c$  for different pressures.  $\circ$ , 0 kbar;  $\Delta$ , 2 kbar. The values of fitted parameters are  $\zeta = -2.7 \times 10^9 \text{ m}^5 \text{ F}^{-1} \text{ C}^{-2}$ , and  $\Delta = 10 \text{ K}$  at 0 kbar and 15 K at 2 kbar.

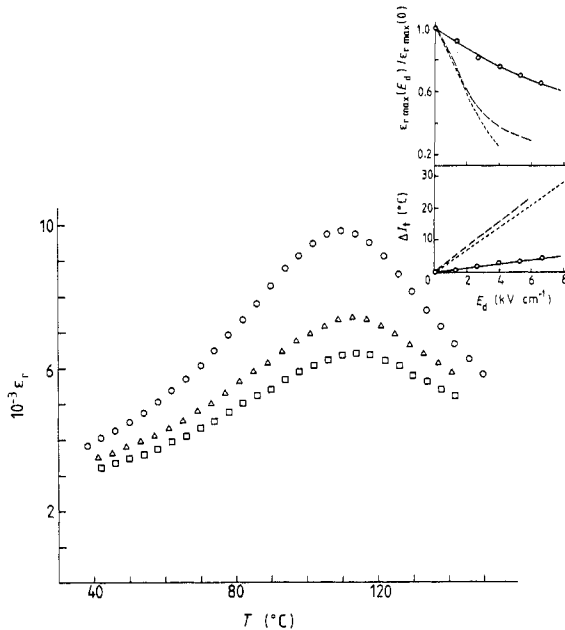
pressure dependence of  $E_c$  is striking while that of  $P_s$  is small. The value of  $P_s$  is calculated from the following equation (Clarke and Burfoot 1974, Yasuda *et al* 1985);

$$P_s = \int_0^\infty P_s(T, \theta) f(\theta) d\theta / \int_0^\infty f(\theta) d\theta \quad (3)$$

where

$$\left. \begin{aligned} P_s(T, \theta)^2 &= -(8\Delta/3C\zeta)\{1 + [1 - \frac{3}{4}(T - \theta'_0)/\Delta]^{1/2}\} & (T < \theta) \\ P_s(T, \theta) &= 0 & (T \geq \theta) \end{aligned} \right\}$$

$\Delta = \theta - \theta'_0$ ,  $\theta'_0 = \theta_0 - Cgp$ ,  $f(\theta)$  is a Gaussian function,  $\exp[-(\theta - T_i)^2/2\sigma^2]$  with a standard deviation  $\sigma$ , describing the distribution for the local Curie temperatures  $\theta$  of microvolume regions around a mean value of  $\theta$  (or the transition temperature  $T_i$ ),  $C$  is the Curie constant,  $g$  the hydrostatic electrostrictive constant,  $\theta_0$  the Curie–Weiss temperature and  $\zeta$  the phenomenological constant. The values of  $P_s$  calculated by computer from equation (3) are shown as full curves in figure 4(a). The value of  $g$  is estimated to be  $1.4 \times 10^{-2} \text{ m}^4 \text{ C}^{-2}$  from the relation  $dT_i/dp = -Cg$  using the values of  $dT_i/dp$  ( $-3.7 \text{ K kbar}^{-1}$ ) and  $C$  ( $2.6 \times 10^{-6} \text{ K F m}^{-1}$ ), estimated from the slope of the  $1/\epsilon_r$  versus  $T$  curve at higher temperatures. The value of  $\sigma$  (20 K) estimated from the  $P_s$  versus  $T$  curve is smaller than that (28 K) estimated from the  $1/\epsilon_r$  versus  $T$  one. These values of  $\sigma$  and  $g$  for PFN are compared with values of  $\sigma$  (39 K) and  $g$  ( $1.2 \times 10^{-2} \text{ m}^4 \text{ C}^{-2}$ ) for PMN with the DPT (Uchino *et al* 1980).



**Figure 5.** The temperature dependence of the relative permittivity  $\epsilon_r$  at 100 kHz for different DC bias fields  $E_d$  at atmospheric pressure.  $\circ$ , 0 kV cm $^{-1}$ ;  $\triangle$ , 3.9 kV cm $^{-1}$ ;  $\square$ , 6.6 kV cm $^{-1}$ . Inset: the decrease in  $\epsilon_{r,max}(E_d)/\epsilon_{r,max}(0)$  and the shift in the temperature  $T_t$  ( $\Delta T_t \equiv T_t(E_d) - T_t(0)$ ) with increasing  $E_d$  PFN compared with  $\cdots$ , PMN and  $---$ , SBN.

### 3.3. Effect of DC bias field

Figure 5 shows the temperature dependence of the relative permittivity  $\epsilon_r$  of PFN at 100 kHz for different DC bias fields up to 6.6 kV cm $^{-1}$  at atmospheric pressure. The effect of DC bias fields on  $\epsilon_r$  is remarkable in the vicinity of the transition temperature  $T_t$ . As the DC bias field  $E_d$  increases, the peak value of  $\epsilon_r$  ( $\epsilon_{r,max}$ ) at  $T_t$  is lowered, its shape becomes more rounded and the  $T_t$  is displaced towards higher temperatures. Such effects of DC bias fields on  $\epsilon_r$  have also been observed for PMN (Bokov and Mylnikova 1961, Verbitskaya *et al* 1971) and Sr $_{0.67}$ Ba $_{0.33}$ Nb $_2$ O $_6$  (SBN) with the DPT (Glass 1969). Both the shift in the temperature  $T_t$  ( $\Delta T_t \equiv T_t(E_d) - T_t(0)$ ), and the decrease in  $\epsilon_{r,max}(E_d)/\epsilon_{r,max}(0)$  with increasing DC bias field  $E_d$  for PFN are shown in comparison with cases of PMN (Bokov and Mylnikova 1961, Verbitskaya *et al* 1971) and SBN (Glass 1969) in the inset in figure 5. The value of  $dT_t/dE_d = 0.7$  K cm kV $^{-1}$  of PFN is much smaller than the 3.5 K cm kV $^{-1}$  of PMN (Bokov and Mylnikova 1961) and 3.9 K cm kV $^{-1}$  of SBN (Glass 1969). The decreasing rate of  $\epsilon_{r,max}(E_d)/\epsilon_{r,max}(0)$  with  $E_d$  for PFN is also small when compared with cases of PMN (Verbitskaya *et al* 1971) and SBN (Glass 1969).

## 4. Summary

The following facts were found for PFN ceramics synthesised via alkoxides: (i) the relative permittivity  $\epsilon_r$  has a broad maximum at the ferroelectric transition temperature  $T_t$ . No dielectric dispersion was observed in the frequency range 1–100 kHz. (ii) Above  $T_t$ ,  $(1/\epsilon_r - 1/\epsilon_{r,max})$  is proportional to  $(T - T_t)^\gamma$ , where  $\epsilon_{r,max}$  is the peak value of  $\epsilon_r$  at  $T_t$  and  $\gamma$  is a constant. The value of the exponent  $\gamma$  was found to be equal to 2.0 and remained almost independent of the applied pressure. (iii) With increasing pressure  $p$ , the values of both  $T_t$  and  $\epsilon_{r,max}$  were reduced. In the case of  $T_t$ , the reduction was linear with  $dT_t/dp = -3.7$  K kbar $^{-1}$ . (iv) Highly saturated polarisation–electric field hysteresis loops

were observed, and the  $T$  and  $p$  dependence of the spontaneous polarisation  $P_s$  and the coercive field was obtained. (v) With increasing DC bias fields  $E_d$ , the  $\varepsilon_{r\max}$  is lowered, its shape becomes more rounded and the  $T_t$  is displaced towards higher temperatures with  $dT_t/dE_d = 0.7 \text{ K cm kV}^{-1}$ . (vi) The  $T$  and  $p$  dependence of the  $\varepsilon_r$  and the  $P_s$  is explained in terms of a phenomenological theory, and the value of the hydrostatic electrostrictive constant was estimated to be  $1.4 \times 10^{-2} \text{ m}^4 \text{ C}^{-2}$ .

No phase transition mechanism to explain such phenomena for the DPT in PFN has been presented.

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