LETTER TO THE EDITOR

The diffuse phase transition in $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics synthesised through the use of alkoxides

Naohiko Yasuda and Yoshitaka Ueda

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

Abstract. Dielectric properties of ferroelectric $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics prepared using alkoxides were measured in the temperature range 30–150 °C. The permittivity shows a broad maximum at the transition temperature T_t and quadratic temperature dependence at temperatures above T_t. The well saturated polarisation–electric field hysteresis loop was observed, and the temperature dependence of the spontaneous polarisation is presented.

Complex perovskite-type ferroelectrics with disordered cation arrangements show the diffuse phase transition (DPT) which is characterised by a broad maximum for the temperature dependence of the permittivity and the dielectric dispersion in the transition region (Smolensky 1970). $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) is a ferroelectric of the disordered type (Smolensky *et al* 1958, Bokov *et al* 1962) which has a ferroelectric transition temperature at 110 °C at atmospheric pressure (Smolensky *et al* 1958, Isupov *et al* 1960, Bokov *et al* 1962). However, it has been reported that PFN does not show a frequency dispersion of the dielectric maximum in the frequency range 100 Hz to 4.5 MHz; instead a nearly normal dielectric behaviour was observed (Isupov *et al* 1960, Shrout *et al* 1984). On the other hand, PFN was reported to have low resistivity (of the order of 10^8 Ω cm at room temperature) (Isupov *et al* 1960). Little has been reported on the temperature dependence of the spontaneous polarisation P_s of PFN. In this work, the breakdown electric field strength is increased by the synthesis of PFN ceramics through the use of alkoxides, making it possible to observe well saturated $P–E$ hysteresis loops (P = polarisation, E = electric field) (see figure 3, later). The value of P_s (6.2 μC cm^{-2} at −136 °C at atmospheric pressure) for PFN ceramics reported previously (Isupov *et al* 1960) is much smaller than the value (13.5 μC cm^{-2}) obtained for the PFN ceramics prepared for this study. Moreover, a strongly broadened permittivity against temperature curve was obtained. In this Letter, the dielectric properties, such as the permittivity and the spontaneous polarisation, of PFN ceramics prepared through the use of alkoxides are presented.

PFN ceramics were prepared using alkoxides. Aqueous benzene solution was added drop by drop into a mixed benzene solution of iron butoxide (reagent grade) and niobium ethoxide (reagent grade) and the resultant precipitate was fired at 1000 °C in air for 1 h to form a wolframite-phase oxide $(FeNb)O_4$. The oxide was mixed with PbO powder (purity 99.99%, particle size <1 μm) 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 °C for 3 h, and sintered at 900 °C for 2 h in a controlled PbO atmosphere in a Pt crucible in
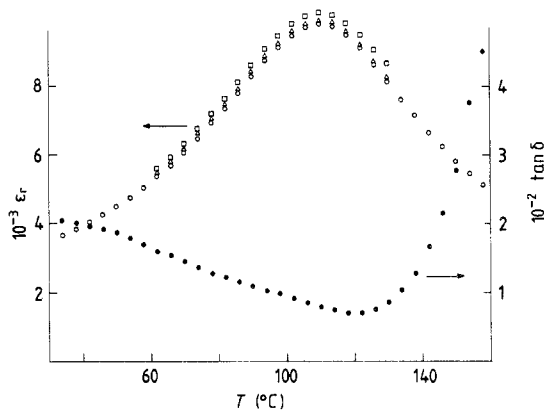
Figure 1. Temperature dependence of the relative permittivity ε_r and the dielectric loss tangent tan δ of $Pb(Fe_{1/2}Nb_{1/2})O_3$. $\square$, 1 kHz; $\triangle$, 10 kHz; $\bullet$, $\bigcirc$, 100 kHz.

order to prevent the loss of PbO. X-ray powder patterns of ceramic specimens showed rhombohedral patterns ($a = 4.017$ Å and $\alpha = 89.57°$) at room temperature as reported previously (Isupov *et al* 1960, Bhat *et al* 1974). The apparent density of the ceramics was 92 to 95% of the theoretical density (8.46 g cm^{-3}). X-ray diffraction confirms that the specimen is 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 °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 V cm^{-1} using an AC bridge, and the spontaneous polarisation was examined with a Sawyer–Tower circuit. All the dielectric data were collected while heating at a rate of 0.5 K min^{-1}. These results were found to be reproducible from sample to sample.

Figure 1 shows the temperature dependence of the relative permittivity ε_r and the dielectric loss tangent tan δ of $Pb(Fe_{1/2}Nb_{1/2})O_3$ at atmospheric pressure. The value of ε_r shows a broad maximum at a temperature T_m (corresponding to the ferroelectric transition temperature T_t), which is independent of frequency from 1 to 100 kHz. The value of T_t at atmospheric pressure (110 °C) is in agreement with that reported previously (Smolensky *et al* 1958, Isupov *et al* 1960, Bokov *et al* 1962).

The dielectric loss peak associated with the dielectric maximum as observed in $Pb(Mg_{1/3}Nb_{2/3})O_3$ with the DPT (Smolensky *et al* 1960) is absent as shown in figure 1. The permittivity of ferroelectrics with the DPT deviates substantially from the Curie–Weiss law at temperatures above T_t. Empirically, the relative permittivity at temperatures above T_t is known to be described by the following relation (Clarke and Burfoot 1974, Uchino and Nomura 1982):

$$1/\varepsilon_r - 1/\varepsilon_{rm} = (T - T_t)^\gamma/C' \tag{1}$$

where ε_{rm} is the maximum value of ε_r, C' the Curie-like constant and γ an exponent. Figure 2 shows logarithmic plots of the reciprocal relative permittivity ($1/\varepsilon_r - 1/\varepsilon_{rm}$) at 100 kHz against the reduced temperature ($T - T_t$) at atmospheric pressure. It is found from the linearity of the curve in figure 2 that equation (1) holds good. The value of γ is determined to be 2.0 from the slope of the straight line in the temperature range $2 < T - T_t < 42$ °C. The Curie-like constant C' is estimated to be 1.7×10^7 from
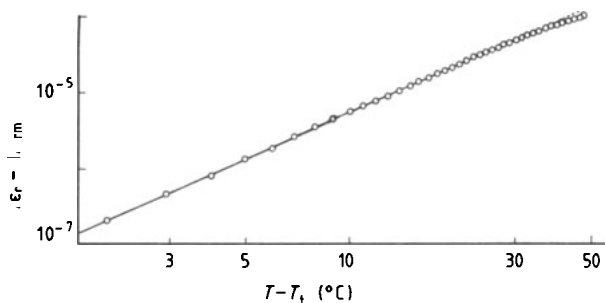
Figure 2. Logarithmic plots of the reciprocal relative permittivity $(1/\varepsilon_r - 1/\varepsilon_{rm})$ at 100 kHz against the reduced temperature $(T - T_t)$ of $Pb(Fe_{1/2}Nb_{1/2})O_3$.

equation (1). Smolensky (1970) has derived the quadratic dependence of ε_r on T on the basis of a microscopic composition fluctuation model.

P–E hysteresis loops with an AC amplitude of 30 kV cm^{-1} and at 60 Hz for different temperatures at atmospheric pressure are shown in figure 3. The maximum polarisation increases with the amplitude of the applied field strength. The P–E hysteresis loop shows a rounded curve. The value of P_s at 30 °C (11.0 μC cm^{-2}) is compared with that at room temperature (12–40 μC cm^{-2}), estimated from the atomic structure of PFN by electron microscopy and x-ray diffraction analysis (Platonov *et al* 1970). With heating, P–E hysteresis loops become narrow and the remanent polarisation very small. Figure 4 shows the temperature dependence of the spontaneous polarisation P_s and the coercive
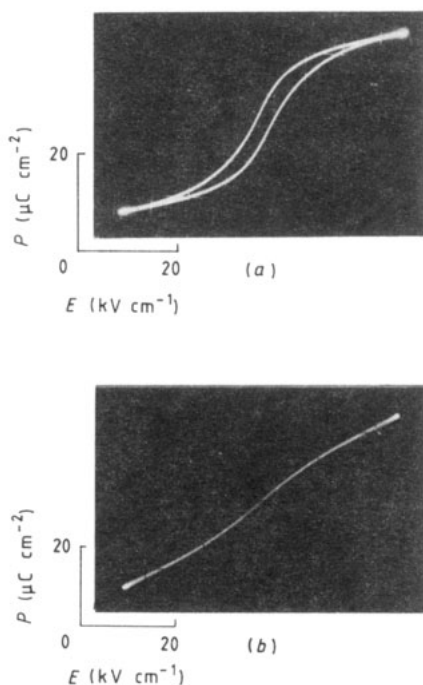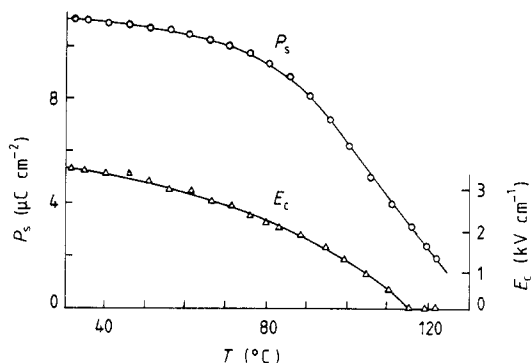

Figure 3. P–E hysteresis loops of $Pb(Fe_{1/2}Nb_{1/2})O_3$.

Figure 4. Temperature dependence of the spontaneous polarisation P_s and the coercive field E_c of $Pb(Fe_{1/2}Nb_{1/2})O_3$.

field E_c obtained from P–E hysteresis loops at atmospheric pressure. With heating, the value of P_s decreases first gradually and then rapidly near T_t. The temperature dependence of E_c is similar to that of P_s. No phase transition mechanism to explain such phenomena for the DPT in PFN (as characterised by the strongly broadened permittivity against T curve and no dielectric dispersion in the frequency range from 100 Hz to 4.5 MHz) has been presented. Further study on PFN under pressure, involving dielectric measurements, is now in progress.

References

Bhat K C, Keer H V and Biswas A B 1974 *J. Phys. D: Appl. Phys.* **7** 2077
Bokov V A, Mylnikova I E and Smolensky G A 1962 *J. Exp. Theor. Phys. USSR, Phys. Ser.* **42** 643
Clarke R and Burfoot J C 1974 *Ferroelectrics* **8** 505
Isupov V A, Agranovskaya A I and Khuchua N P 1960 *Bull. Acad. Sci. USSR, Phys. Ser.* **24** 1268
Platonov G L, Drobyshev L A, Tomashpolskii Yu Ya and Venevtsev Yu N 1970 *Sov. Phys.–Crystallogr.* **14** 692
Shrout T R, Swartz S L and Haun M J 1984 *Ceram. Bull.* **63** 808
Smolensky G A 1970 *J. Phys. Soc. Japan* **28** 26
Smolensky G A, Agranovskaia A I, Popov S N and Isupov V A 1958 *Sov. Phys.–Tech. Phys.* **3** 1981
Smolensky G A, Isupov V A, Agranovskaya A I and Popov S N 1960 *Fiz. Tverd. Tela* **2** 2906
Uchino K and Nomura S 1982 *Ferroelectrics* **44** 55