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LETTER TO THE EDITOR

Diffuse first-order phase transition in $\text{NaNbO}_3\text{:Gd}$ **I P Raevski¹, S I Raevskaya¹, S A Prosandeev¹, V A Shuvaeva²,
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Abstract

Dielectric permittivity measurements show that $(1-x)\text{NaNbO}_3-(x)\text{Gd}_{1/3}\text{NbO}_3$ crystals, at $x = 0.09$, exhibit a first-order phase transition near 150°C that is diffuse over a wide temperature interval. The area of the $\varepsilon'(T)$ thermal hysteresis loop was found to depend both on annealing and cooling temperatures. Optical studies in polarized light show a decrease of the domain sizes at this phase transition. The results obtained are fitted assuming a spatial distribution of Curie temperatures.

1. Introduction

Although diffuse phase transitions have been known for a long time in ferroelectric relaxors [1, 2], they have not been studied much in perovskite-based antiferroelectrics [3–5]. However, the latter have some obvious advantages in technical applications because of the absence of toxic lead and the strong frequency dispersion of the dielectric permittivity inherent in relaxors. In the present study, we discuss a new material, $\text{NaNbO}_3\text{:Gd}$, that shows some intriguing properties.

On cooling from high temperature, pure NaNbO_3 exhibits a series of six phase transitions from the high-temperature paraelectric cubic phase (space group $Pm\bar{3}m$) through different non-ferroelectric phases (denoted T_2 , T_1 and S), through two antiferroelectric (AFE) phases (R and P , space groups $Pmnm$ and $Pbma$, respectively) to a low-temperature ferroelectric phase N (space group $R3c$) [6, 7]. The P – R transition is accompanied by a sharp maximum in dielectric permittivity between 350 and 370°C . This phase transition is of first order and is characterized by a comparatively narrow (about 10 K) thermal hysteresis in $\varepsilon'(T)$ (figure 1, curve 1). Note that hereafter we shall use the term ‘hysteresis’ to mean thermal hysteresis.

Solid solutions of NaNbO_3 with KNbO_3 and LiNbO_3 have been intensively studied over the last three decades. They exhibit sharp ferroelectric phase transitions and are widely used as high-frequency piezoelectric ceramics [1, 8]. In contrast, it has been found recently that some other solid solutions based on NaNbO_3 exhibit *diffuse* phase transitions [3]. In particular, when

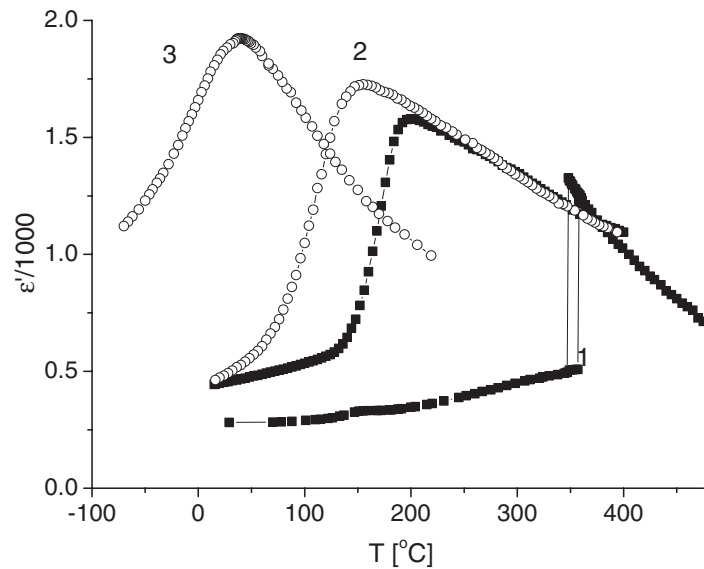


Figure 1. Dielectric permittivity in NNG0 (1), NNG9 (2) and NNG12 (3) measured at 100 kHz. The number after NNG shows the concentration of $\text{Gd}_{1/3}\text{NbO}_3$ in mol%.

doped with Gd (below we use the notation NNG for these solid solutions), NaNbO_3 shows a large increase (up to 100 K) in hysteresis (see also [9, 10] where similar phenomena have been observed in other AFE compositions, $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ and solid solutions based on AgNbO_3). At $x \approx 0.1$, NNG exhibits a jump to a state where the hysteresis disappears (figure 1, curve 3). A qualitative explanation of this phenomenon has been given in terms of stresses and fields introduced by Gd [11].

In the present study, we consider whether the diffuseness of the phase transition found earlier in NNG12 [3] (see caption to figure 1 for the notation) is special for this composition alone, where there is no hysteresis, or whether it occurs also at lower Gd concentrations, where the phase transition shows a large hysteresis and is of first order. If this is the case, then a study of this type of *diffuse first-order* phase transition may lead to a new branch of ferroelectrics and antiferroelectrics, hitherto unreported.

The study of diffuse first-order phase transitions is also of general interest: in some new materials (e.g. doped lanthanum manganate perovskites) exhibiting giant magnetoresistance, some features of a diffuse second-order phase transition were observed together with signs of a first-order phase transition [12, 13]. Another example is offered in the field of biophysics, where it has been observed that lipid membranes experience a diffuse first-order phase transition from the liquid to the solid state [14]. Solid solutions of relaxors with normal ferroelectrics, like $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$, that exhibit promising electrostrictive properties, show a sharp first-order phase transition at a large PbTiO_3 concentration, which disappears at smaller concentrations. It has also been suggested that one should consider athermal martensitic phase transitions as being diffuse first-order in character [15].

2. Experiment

NNG crystals were grown by the flux method using the $\text{Na}_2\text{CO}_3\text{-Nb}_2\text{O}_5\text{-B}_2\text{O}_3$ system with additions of Gd_2O_3 . The crystals were roughly cubic in shape (edge dimensions 0.5–2 mm)

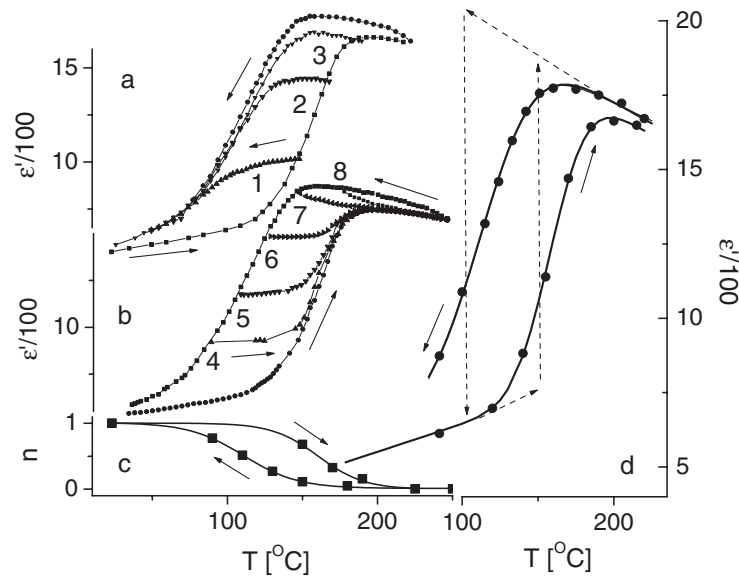


Figure 2. Experimental data on dielectric permittivity of NNG9 obtained (a) for different annealing temperatures: T_a ($^{\circ}\text{C}$) = 150 (1), 170 (2), 190 (3); (b) different cooling temperatures: T_{cool} ($^{\circ}\text{C}$) = 90 (4), 110 (5), 130 (6), 150 (7), 180 (8); (c) the low-temperature-phase fraction, n , obtained from experiment (squares); solid curves and dashed lines are guides for the eye; (d) comparison of the fit of expression (2) (solid curve) to experimental data (circles). Dotted curves show normal first-order phase transition behaviour. The angles between the dashed lines and solid curves characterize the degree of diffuseness of the phase transition.

with sides parallel to the (100) planes of the perovskite prototype structure. Full details of the preparation of the crystals and their characterization have been described elsewhere [3, 16]. Aquadag electrodes were deposited on opposite faces of the as-grown crystals, and dielectric measurements were carried out in the course of both heating and cooling at a rate about $(2\text{--}3)\text{ K min}^{-1}$.

Figures 2(a) and (b) show the results of thermo-cycling experiments for a NNG9 crystal: the first group of measurements included heating of the crystal up to $T = T_a$ with subsequent cooling to low temperatures (figure 2(a)). In the second group of experiments (figure 2(b)), we varied the cooling temperature T_{cool} . It can be seen that the form of the hysteresis depends on T_a and T_{cool} strongly. We have observed qualitatively similar effects for other solid solutions of NaNbO_3 (single crystal and ceramic) exhibiting a large temperature hysteresis of $\varepsilon(T)$. To elucidate the role of kinetics in the observed phenomena, we carried out ageing experiments at several temperatures between T_a and T_{cool} . For ageing times of less than 10^2 s (this corresponds to the heating/cooling rate of 0.1 K min^{-1} that we have used in order to obtain an accuracy in temperature stabilization of about 0.1 K) no noticeable changes were found. For ageing times exceeding 10^3 s , some changes were observed for compositions showing the largest values of thermal hysteresis ($100\text{--}120\text{ K}$) at temperatures close to the $\varepsilon(T)$ maximum during cooling. Even after $10\text{--}20\text{ h}$ ageing neither the width of the thermal hysteresis nor the slope of the low-temperature side of the maximum in $\varepsilon(T)$ changed substantially. Full details of the ageing behaviour will be the subject of a separate publication.

The results presented in figure 2 show that the first-order phase transition in NNG9 develops step by step in finite volumes. Indeed, if the phase transition were sharp then one would expect the form of the hysteresis to be reversible in the sense that the experimental points would

follow the same path independently of T_a and T_{cool} . What one sees is a result of the fact that, at each temperature near the phase transition, some parts of the crystal are in the low-temperature (LT) phase, and some in high-temperature (HT). On heating the crystal after cooling, the LT parts of the crystal switch to the HT phase. This is accompanied by hysteresis, the area under which increases with increase of the LT phase fraction, $n(T_{cool})$. Similarly, on cooling the crystal after heating, the hysteresis area decreases with increase of $n(T_a)$. Hence the phase is inhomogeneous at the diffuse phase transition.

The problem of describing dielectric permittivity in inhomogeneous media is usually discussed in terms of the effective medium approximation [17], within which we find that the fraction of the low-temperature (LT) phase is given by:

$$n(T) = \frac{[\varepsilon_2(T) - \varepsilon'(T)][\varepsilon_1(T) + 2\varepsilon'(T)]}{3\varepsilon'(T)[\varepsilon_2(T) - \varepsilon_1(T)]} \quad (1)$$

where $\varepsilon_1(T)$ and $\varepsilon_2(T)$ are the dielectric permittivities in the LT- and HT-phases, respectively. All these quantities can be obtained from our experiment. In agreement with our initial assumption, the $n(T)$ dependence (figure 2(c)) is diffuse. One can also use the hysteresis area as a (non-linear) measure of $n(T_{cool})$ on cooling and $1 - n(T_a)$ on heating. Below, we discuss the shape of $n(T)$ in more detail.

Temperature-dependent optical studies of NNG were also carried out by the rotating polarizer method, using the Metripol (www.metripol.com) microscope system [18] and a precise heating stage (Linkam HFS91). False-colour images showing values of $|\sin \delta| = |\Delta n L 2\pi / \lambda|$ (Δn —birefringence, L —crystal thickness, λ —light wavelength) and the orientation of the optical indicatrix at every point of the crystals were obtained in the temperature range 20–600 °C in 0.5° steps. NNG crystals with $x = 0.02$ –0.09 display distinctive changes of birefringence with temperature similar to that in NaNbO_3 , which can be attributed to an antiferroelectric phase transition. At the phase transition point, a spontaneous splitting into small regions (<0.001 mm in size) with diffuse boundaries occurs, and the distribution of the birefringence image becomes very complex. Well away from the phase transition the scale of this non-uniformity increases up to 0.05 mm.

3. Discussion

Phase transitions in antiferroelectrics may be accompanied by dielectric anomalies because of coupling between AFE and ferroelectric order parameters. In a first-order phase transition, the AFE order parameter experiences a jump and, as a result, the dielectric function exhibits a step. Figure 2(d) shows $\varepsilon'(T)$ obtained for NNG9. The dashed lines show the dependence that one would expect if the phase transition were not diffuse. The sharp steps in the cooling and heating runs are separated because of hysteresis. The experimental points correspond rather to a diffuse first-order phase transition: the steps are diffuse over some temperature interval. In order to describe this diffuseness, one can introduce a distribution function for the Curie temperatures, $f(T_c)$, which, in the simplest case, may be described by a Gaussian function (this distribution originates from internal local fields and stresses introduced by impurities [11, 15]):

$$\varepsilon'(T) = \varepsilon_0(T) + b(T) \int f(T_c) \theta(T - T_c) dT_c = \varepsilon_0 + B \text{erf}[(T - T_{c0})/\Gamma] \quad (2)$$

where $\varepsilon_0(T)$ and $B(T)$ are monotonic functions of temperature, which, in the first approximation, can be given by linear functions. Note that the Curie temperature of the ferroelectric phase transition is sufficiently lower than the temperature of the step. $\theta(x)$ is a step function, which equals 0 at $x < 0$ and 1 at $x > 0$; $\text{erf}(x)$ is the error function.

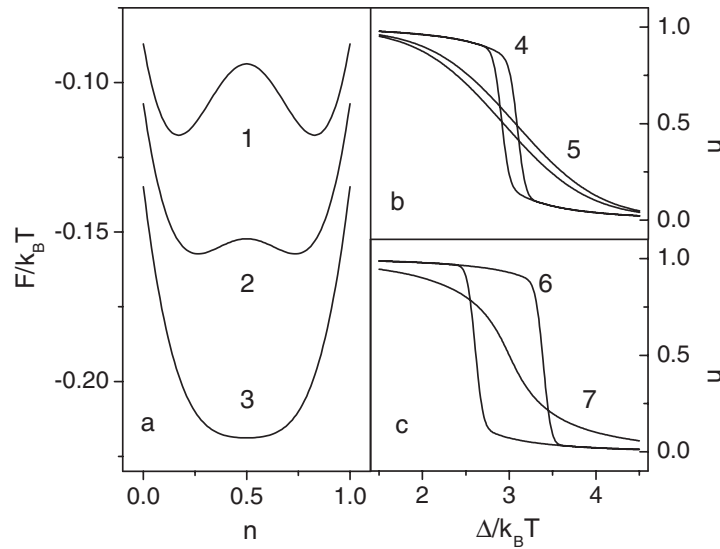


Figure 3. Theoretical curves for the model free energy (a): 1—(2.4, 0.1); 2—(2.4, 1.0); 3—(2.4, 1.5); and order parameter n (b), (c): 4—(2.4, 0.1); 5—(2.4, 1.0); 6—(3.0, 0.1); 7—(1.5, 0.1). (The values in parentheses are $\gamma z/k_B T$ and $a/k_B T$.)

The fit (solid curves in figure 2(d)) shows that the width of the distribution function for NNG9 is about 27 K on heating and 35 K on cooling, which is nearly comparable with the hysteresis width, 44 K. We found that the distribution function width decreases with decrease of the Gd concentration. For pure NaNbO_3 , the width of the distribution function is negligible.

The results obtained indicate that the disappearance of the hysteresis and the dramatic increase of the diffuse behaviour in $\varepsilon'(T)$ observed experimentally [3] in NNG12 (see figure 1), may be due to a crossover between the widths of the $\varepsilon'(T)$ hysteresis and the Curie temperature distribution function. This implies that, at this concentration, and over a wide temperature interval, there are intermediate states, which help the continuous phase transition to proceed.

The diffuseness of a first-order phase transition means coexistence of more than one phase (two in our case). This must increase the surface tension energy, which opposes this coexistence. Analogously, in relaxors the depolarization energy is opposed by the appearance of polar regions [11]. There must therefore be some means by which this energy increase can be compensated. Below, we discuss the surface tension contribution to the energy within a microscopic approach [19, 20].

We supplemented the approach [19] by spreading the chemical potential over temperature with a Gauss distribution function with the width a . We found that increasing a decreases the barrier height between the states (figure 3(a)). Thus, the energy barriers (the energy gain) mediated by the surface tension is compensated by the spatial distribution of Curie temperature.

Figures 3(b) and (c) show the shape of the $n(T)$ dependence for different model parameters: the surface tension γ , number of nearest neighbours in the lattice z and width a . One can see that by decreasing the slope of the $n(T)$ dependence at the phase transition, when a increases (figure 3(b)), the form of the hysteresis becomes stretched and thin. Hence, this slope can be used as a measure of the sharpness of the phase transition. Figure 3(c) shows a similar tendency when one decreases the surface tension: decreasing γ decreases the hysteresis area and decreases the slope of the $n(T)$ dependence.

Thus, the increase of a and/or decrease of γ decreases the average energy barrier between the phases and decreases the slope of the $n(T)$ dependence. The real situation is more complex because of the random distribution of barriers in space (the decrease of the barriers may result in percolation of the new phase, as has been found for manganates [12]), but the model does give a reasonable explanation of the observed behaviour: the phase transition is diffuse in spite of the surface tension, the role of which is suppressed because of spreading of the Curie temperature.

The experimental measurements shown above have demonstrated that the first-order phase transition in the NNG crystals is diffuse in the sense that, over a wide temperature interval, two phases (stable far above and below the phase transition temperature) coexist. This coexistence was clearly confirmed by the experiments in which we varied T_a and T_{cool} . These results are also consistent with the optical studies performed, showing a dramatic decrease of the average domain size with increase of Gd content. Thus, we have found that there is a large diffuseness of the dielectric permittivity in both cases, NNG9 and NNG12, where thermal hysteresis is large and where it is absent. Both the hysteresis width and diffuseness of dielectric permittivity are controlled by the Gd content. The large hysteresis can be explained by internal stresses introduced by Gd [3]. The large diffuseness makes sense as a consequence of decreasing the sizes of domains and spreading of the Curie temperature over a wide temperature interval. The temperature of the phase transition can easily be tuned by further additions of foreign ions [3], such as Li or K, and can be shifted into a temperature interval where technological applications would become viable.

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