New, Lead Free, Perovskites With a Diffuse Phase Transition: NaNbO$_3$ Solid Solutions

I. P. Raevski and S. A. Prosandeev

Department of Physics, Rostov State University, 5 Zorge Street, 344090, Rostov on Don, Russia

Abstract. Some of $(1-x)$NaNbO$_3-(x)$ABO$_3$ perovskite solid solutions exhibit a dramatic diffusion of the dielectric permittivity $\varepsilon'$ maximum and relaxor-type behavior when the second component concentration exceeds a threshold value $x_0$. The concentration phase transition to the relaxor-like phase is abrupt (of the first order kind) that is seen from the step in the dependence of the $\varepsilon'(T)$ maximum temperature, $T_m$, on $x$. The precursor of this transition is a giant (up to 100 K) temperature hysteresis of $\varepsilon'(T)$. Some relaxor-like properties appear even at $x < x_0$ in the course of cooling while disappear in the course of heating. The experimental data obtained are qualitatively described within a Landau-type phenomenological approach, assuming the relaxor-type behavior to be local stress-induced.

I INTRODUCTION

The relaxor behavior in perovskites was studied predominantly in Pb-containing ternary compounds (PMN, PST, PSN) and solid solutions (PLZT, PMN-PT) [1-3]. Last years some lead-free BaTiO$_3$-derived solid solution compositions attracted much attention as environmentally benign relaxor materials [4]. However up to now the obtained values of the dielectric permittivity $\varepsilon'$ maximum temperature, $T_m$, in the BaTiO$_3$-based relaxors were too low for potential applications [4]. The aim of the present paper is studying the dielectric properties of some NaNbO$_3$-based solid solutions forming a new family of lead-free materials with diffuse phase transition (DPT).

On heating NaNbO$_3$ exhibits a series of six phase transitions from the low temperature ferroelectric (FE) phase $N (R3c)$ to the high temperature paraelectric (PE) cubic phase $U (Pm3m)$ through different antiferroelectric (AFE) and PE phases [5]. An $\varepsilon(T)$ maximum originating from the first order transition between two AFE phases: $P (Pbma)$ and $R (Pmmn)$ is observed at 350-370°C.

Similar to solid solutions of other perovskite antiferroelectrics, the NaNbO$_3$-ABO$_3$ binary solid solution systems can be divided into two groups [6]. In the solid solutions of group I (e.g. (Na,Li)NbO$_3$ and (Na,K)NbO$_3$ systems) the high
temperature FE phase appears at small (a few mol.%) content $x$ of the second component $ABO_3$, the $T_m(x)$ dependence is rather smooth and the $\varepsilon'(T)$ maxima are sharp. In the solid solutions of group II the AFE phase remains stable up to a comparatively high $x$ values. In contrast to the solid solutions of other perovskite antiferroelectrics, the $T_m(x)$ dependence of the NaNbO$_3$-based group II solid solutions remains smooth only up to a threshold $x = x_0$ value. At $x > x_0$ the phase, usually referred to as FE (though sometimes it is supposed to be ferrielectric), becomes stable, which is accompanied by an abrupt drop in the $T_m$ values and dramatic diffusion of the $\varepsilon'(T)$ maximum. While the $T_m$ values of the compositions with $x < x_0$ do not depend on frequency, the compositions with $x > x_0$ were reported to exhibit a frequency dispersion of $\varepsilon'$ and an increase of $T_m$ with frequency [6]. Thus, it seems that NaNbO$_3$-based solid solutions belonging to group II exhibit a relaxor-like behavior at $x > x_0$. Besides, the lack of systematic data on the properties of such materials prevents one from definite conclusions. Below we will consider some group II NaNbO$_3$-based solid solutions dielectric properties dependence on the concentration of the second and third components as well as on temperature and frequency.

II EXPERIMENTAL RESULTS

NaNbO$_3$-Gd$_{1/3}$NbO$_3$ solid solution crystals were grown by the flux method. The details of crystal preparation and characterization have been described elsewhere [7]. The ceramic samples of NaNbO$_3$-based solid solutions were prepared by routine solid-state reaction route. The density of the obtained ceramics was about 90-95% of theoretical one. For dielectric measurements Aquadag electrodes were deposited on the opposite faces of the as-grown crystals, while Ag paste was fired to the grinded disk surfaces of ceramic samples. The dielectric studies were carried out in the 1 kHz - 1 MHz range in the course of both heating and cooling at a rate of 2 - 3°C/min with the aid of the R5083 and E7 – 12 capacitance bridges.

Fig. 1 shows the typical evolution of the $\varepsilon'(T)$ dependencies with the composition for the solid solution of group II. The similarity of the data obtained for ceramic samples and crystals shows that the peculiar properties of the group II solid solutions are not due to the immiscibility effect typical of many solid solution ceramics. A strong frequency dispersion of both real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of complex dielectric permittivity observed at temperatures exceeding $T_m$ or $T_m'$ (Fig. 2) is likely to be caused by a decrease of the conductance influence with increasing frequency. Though the $\varepsilon'(T)$ maxima of the group II NaNbO$_3$-based solid solution compositions with $x > x_0$ are smeared and a frequency dispersion of $\varepsilon'$ is observed, the shift of $T_m$ with frequency is usually much smaller than in the case of PbMg$_{1/3}$Nb$_{2/3}$O$_3$-type relaxors (Fig.2). Similar to other FE and AFE with DPT [1-3], the permittivity of NaNbO$_3$-based solid solution compositions with $x > x_0$ does not follow the Curie-Weiss law in a broad temperature range above $T_m$ (Fig. 2) while at higher temperatures the Curie-Weiss behavior is observed. It
is well documented that in FE with DPT the extrapolated Curie-Weiss temperature of the FE phase transition, \( T_{CW} \), is necessarily higher than \( T_m \) due to a large contribution to the high-temperature permittivity from the regions that have a higher transition temperature [1-3]. In contrast to this, in all the group II NaNbO_3-based solid solutions studied, the \( T_{CW} \) values are much lower than \( T_m \) (Fig. 2). Figure 3 shows the concentration dependencies of \( T_m \) measured on heating for some solid solutions belonging to group II. It is interesting to note that for many solid solution systems of group II the linear extrapolations of the \( T_m - x \) diagram portions from the \( x > x_0 \) region intersect at the same point \((x = 0, T \sim 150^\circ C)\) corresponding to the minor \( \varepsilon'(T) \) anomaly often observed in NaNbO_3 [8].

![Figure 1](image-url)

**FIGURE 1.** Evolution of the \( \varepsilon'(T) \) dependencies measured on heating and subsequent cooling with composition for \((1-x) \text{NaNbO}_3-x\text{Gd}_{1/3}\text{NbO}_3\) single crystals (solid lines) and ceramics (dashed lines). Figures correspond to \( x \) values.

A specific feature of the group II solid solutions is an anomalously large value of the thermal hysteresis \( \Delta T_h \) of the \( \varepsilon'(T) \) dependence typical of the compositions with \( x < x_0 \). The \( \Delta T_h \) values increase with \( x \) and in some systems exceed 100 K for compositions adjacent to \( x_0 \) (Figs. 1, 4). The concentration dependence of \( \Delta T_h \) is substantially nonlinear (Fig. 4). When a small amount of FE third component is added to the given solid solution, \( \Delta T_h \) values usually increase [10-12]. At higher FE component content the \( \Delta T_h \) values decrease dramatically [11]. If the temperature is stabilized in the course of cooling within the thermal hysteresis range the temporal changes in \( \varepsilon' \) do not exceed a few % during several hours [12]. Application of DC bias on compositions exhibiting giant \( \Delta T_h \) values does not change the \( \varepsilon'(T) \) curve measured in the heating mode while in the course of subsequent cooling some lowering of the \( \varepsilon'(T) \) maximum was observed [12,13]. Anomalously large values of \( \Delta T_h \) were observed both in the ceramics and single crystals and can serve as an experimental evidence of the fact that the given solid solution belongs to group II [7,9,11]. It is worth noting that in perfect NaNbO_3 single crystals the \( \Delta T_h \) value does not exceed 10 K, but increases substantially with
FIGURE 2. Temperature dependencies of $\varepsilon'(1'-3')$, $\varepsilon'' (1''-3'')$ and $10^6/\varepsilon'$ (3) measured at 1 kHz (1',1''), 10 kHz (2',2'') and 100 kHz (3,3',3'') for 0.88NaNbO$_3$-0.12Gd$_{1/3}$NbO$_3$ single crystal.

FIGURE 3. Concentration dependencies of the $\varepsilon'(T)$ maximum temperature $T_m$ measured on heating for some NaNbO$_3$-based solid solutions belonging to the group II (1-5) as well as for 0.88 NaNb$_{1-x}$Ta$_x$O$_3$-0.12LiNbO$_3$ [16] system (6). The second components of the solid solutions are: 1. BiFeO$_3$; 2. SrCu$_{1/3}$Nb$_{2/3}$O$_3$; 3. CaTiO$_3$ [17]; 4. SrTiO$_3$ [23]; 5. NaTaO$_3$[24];
the increase of the oxygen vacancy concentration [14]. In nominally stoichiometric NaNbO$_3$ ceramics the $\Delta T_h$ values of 30 - 40 K are usually observed (Fig. 1). These larger values of $\Delta T_h$ in ceramic samples are likely to be attributed to a high point-defect concentration, e.g. due to evaporation of Na$_2$O during sintering. Indeed, in Na$_2$O-deficient Na$_{1-x}$NbO$_{3-x/2}$ ceramics [15] the $\Delta T_h$ values are substantially larger than in the nominally stoichiometric ones. Both the oxygen- and Na$_2$O -deficiency leads to an increase of the $T_m$ values in NaNbO$_3$ [14,15] and an almost linear correlation of $\Delta T_h$ and $T_m$ is observed.

**FIGURE 4.** Concentration dependence of the $\varepsilon'(T)$ maximum temperature $T_m$ measured on heating (1) and on cooling (2) as well as the $\varepsilon'(T)$ temperature hysteresis $\Delta T_h$ values (3) for (1-x)NaNbO$_3$-xGd$_{1/3}$NbO$_3$ crystals (open symbols) and ceramics (filled symbols).

**FIGURE 5.** Changes in the $\varepsilon'(T)$ dependencies of 0.8NaNbO$_3$-0.2Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (1) and NaNb$_{0.45}$Ta$_{0.55}$O$_3$ (2) solid solution ceramics caused by addition of 10 mol% of LiNbO$_3$ (curves 1a and 2a) or KNbO$_3$ (1b). Curve 2a is drawn using the data of Ref. [16].

It should be mentioned that a noticeable step in the $T_m(x)$ dependence of the
NaNbO$_3$-based solid solutions belonging to group II is observed only for the $T_m$ values measured in the heating mode. If $T_m$ is determined from the $\varepsilon'(T)$ dependence measured in the course of cooling, the $T_m(x)$ curve is rather smooth (Fig. 4). The $\varepsilon'(T)$ dependencies measured in the cooling mode are usually more diffused as compared to those measured upon heating (Fig. 1). Moreover, just at the step in the $T_m(x)$ dependence the $\varepsilon'(T)$ curve obtained on cooling down has a relaxor-like diffuse maximum that can imply that the relaxor-type state had been already appeared in a metastable thermodynamic state occupied at cooling. The stability of this state arises at temperatures lower than the step in the $T_m(x)$ dependence. In the latter case (i.e. for the compositions with $x > x_0$) the curves obtained in the cooling and heating modes practically coincide.

As one can see from Figs. 1 and 3, the $T_m$ values of the known binary NaNbO$_3$-based relaxor-type solid solutions, belonging to group II, are usually well below the room temperature, and the maximal $\varepsilon'$ values, $\varepsilon'_m$, are much lower than in the Pb-containing relaxors. However, in the ternary NaNbO$_3$-NaTaO$_3$-LiNbO$_3$ solid solution system a dramatic increase in both the $T_m$ and $\varepsilon'_m$ values with the LiNbO$_3$ content is observed [16] for the compositions from the $x > x_0$ range (Figs. 3 and 5). Similar behavior is typical of other NaNbO$_3$-based solid solutions (Fig. 5).

**III DISCUSSION**

When discussing the experimental data we will use a phenomenological Landau-type approach. For the sake of simplicity we do not follow the complex symmetry of the NaNbO$_3$-based solid solutions but rather, in order to make a qualitative description, we consider a simplified case when there are two nonpolar (AFE) ($Q_1$, and $Q_2$) and one polar (FE) ($P$) order parameters. An important constraint on the Free energy expansion is that an AFE phase transition may exhibit a peak or step in the $\varepsilon'(T)$ only because of coupling between FE and AFE order parameters [18,19]. The impurities we consider are expansive that implies that they produce local random stress ($\sigma_l$) leading to a local expansion of the lattice parameter and, hence, to local strain ($\varepsilon$). The small observed dispersion of $\varepsilon'(T)$ at $x > x_0$ requires the introduction of an additional parameter ($d$), which is the local mean square impurity-induced dipole (or multipole) moment. We assume that local expansion around a defect may lead to noncentrosymmetric relaxations of neighboring atoms yielding a net local moment, or a multipolar set of local moments. Averaged over the whole crystal, these relaxations do not generate a net macroscopic moment but local moments cause dispersion of $\varepsilon'(T)$. Extended dipole-dipole interactions are assumed to be sufficiently weak that they can be ignored.

We expand the Free energy as a sum of $x$-independent ($F_1$) and $x$-dependent ($F_2$) contributions, $F = F_1 + xF_2$ where
\[ F_1 = F_0 + \frac{1}{2} \alpha_1 (T) P^2 + \frac{1}{4} \beta_1 Q^4 - EP + \frac{1}{2} \alpha_{21} (T) Q_1^1 + \frac{1}{3} \beta_{21} Q_1^1 + \frac{1}{2} \beta_{22} Q_2^2 + \frac{1}{4} \gamma_{21} Q_1^6 + \frac{1}{2} \beta_{121} P^2 Q_1^1 + \frac{1}{2} \beta_{122} P^2 Q_2^2 \]

\[ F_2 = \frac{1}{2} c_e e^2 - \sigma_1 e - \frac{1}{2} a_1 e P^2 + \frac{1}{2} a_{21} e Q_1^1 + \frac{1}{2} a_{22} e Q_2^2 - \lambda d e + \frac{1}{2} \kappa d^2 \]

Here \( \alpha_i = c_1 (T - T_1^{(0)}) \), \( \alpha_{2i} = c_{2i} (T - T_2^{(0)}) \), \( T_1^{(0)} \) and \( T_2^{(0)} \) are the bare Curie temperatures for the FE and AFM phase transitions respectively, \( E \) is external electric field, \( e \) is the symmetrical part of the strain tensor. From the equilibrium condition with respect to \( e \) and \( d \) one has

\[ e = \frac{1}{c_L} \left( \sigma_1 + \frac{1}{2} a_1 P^2 - \frac{1}{2} a_{21} Q_1^1 - \frac{1}{2} a_{22} Q_2^2 \right) \]

It implies that \( d \) multiplied by \( \lambda \) plays the role of the local stress and hence it effectively enlarges the local stress produced by impurities, \( d \) proves to be proportional to the strain \( e \). From (1) and (2) one can easily find that \( e \) (as well as \( d \), see [20]) is enhanced due to mutual coupling between \( e \) and \( d \):

\[ e = \frac{1}{c_L - \lambda^2 / \kappa} \left( \sigma_1 + \frac{1}{2} a_1 P^2 - \frac{1}{2} a_{21} Q_1^1 - \frac{1}{2} a_{22} Q_2^2 \right) \]

By using (3) one can rewrite Free energy in the simple form containing expansions only with respect to \( P \) and \( Q \):

\[ F = F'_0 + \frac{1}{2} A_1 (x, T) P^2 + \frac{1}{4} B_1 (x) P^4 - EP + \frac{1}{2} A_{21} (x, T) Q_1^1 + \frac{1}{2} A_{22} (x, T) Q_2^2 - \frac{1}{4} B_{21} (x) Q_1^1 + \frac{1}{4} B_2 (x) Q_2^2 + \frac{1}{4} G_2 (x) Q_2^6 + \frac{1}{2} B_{121} (x, T) P^2 Q_1^1 + \frac{1}{2} B_{122} (x, T) P^2 Q_2^2 + ... \]

where \( F'_0 = F_0 - x \sigma_1^2 / 2 \varsigma \) and coefficients \( A \) and \( B \) depend on concentration, e.g.

\[ B_{21} (x) = \beta_{21} + x a_{21} / 2 \varsigma \]
\[ B_{121} (x) = \beta_{121} + x a_{121} / 2 \varsigma \]
\[ B_{122} (x) = \beta_{122} + x a_{122} / 2 \varsigma \]

Here \( \varsigma = (c_L - \lambda^2 / \kappa) / c_L \). We have obtained that the coupling of the order parameter \( Q \), with the strain \( e \) produced by the impurities leads to the dependence of the coefficients in the Landau expansion on the concentration \( x \) (see also [21]).

Composition dependence in coefficients (5) implies that the Curie temperature also depends on \( x \):

\[ T_1 = T_1^{(0)} + x \sigma_1 a_1 / c_1 \varsigma \]
\[ T_{2i} = T_{2i}^{(0)} - x \sigma_1 a_{2i} / c_{2i} \varsigma \]

From these expressions it is seen that if \( a_1 > 0 \) and \( a_2 > 0 \) then \( T_1 \) increases with \( x \) and \( T_2 \) decreases with \( x \) linearly. The latter result corresponds to the
experimental data: all group II NaNbO$_3$-based solid solutions studied exhibit a decrease in $T_m$ with $x$. The assumed signs of $a_1$ and $a_2$ are natural as the electrostrictive constant $a_1$ is always positive (if in the F one puts the sign “-” in front of it) and $a_2$ should also be positive (if one puts the sign “+” in front of it) because compression of the lattice ($e < 0$) typically promotes AFE order while the expansion ($e > 0$) promotes FE order.

From expansion (4) one can easily obtain: the critical temperature of the AFE phase transition, $T_{A_i}$; the temperature hysteresis width, $\Delta T_h$; and the jump of the AFE order parameter, $\Delta Q_1$:

$$
T_{A1} = T_{21} + 3B_{21}^2/16c_{21}\gamma_{21} - B_{121}P^2/c_{21}
$$
$$
T_{A2} = T_{22} - B_{122}P^2/c_{22}
$$
$$
\Delta T_h = B_{21}^2/4c_{21}\gamma_{21}
$$
$$
\Delta Q_1 = \sqrt{B_{21}/2\gamma_{21}}
$$

From (6) it is clear that $T_{2i}$ is a linear function of $x$, which implies that $T_{A_i}(x)$ is also linear at small $x$. This corresponds to the experimentally observed linear decrease of $T_m(x)$ with $x$ both above and below $x_0$ as well as explains why linear extrapolations to the point $x = 0$ for various second components, intersect at one point (Fig. 3). These points correspond to the bare Curie temperatures $T_{2i}^{(0)}$. The slopes of the linear dependencies above and below $x_0$ are different as are the electrostriction constants ($a_{21} > a_{22}$). Thus: Curie lines $T_{A1}(x)$ and $T_{A2}(x)$ intersect at $x = x_0$; $Q_1$ is nonzero for $T < T_{A1}$ ($x < x_0$); $Q_2$ is nonzero for $T < T_{A2}$ ($x_0 < x$). The point $x = x_0$ can be found from the equality: $T_{A1}(x) = T_{A2}(x)$.

At the intersection of curves $T_{A1}(x)$ and $T_{A2}(x)$, the first order phase transition to the AFE phase, with order parameter $Q_1$, intersects the second order phase transition to the AFE phase, with order parameter $Q_2$, at a critical endpoint [22]. The principle experimental evidence supporting this interpretation is that the thermal hysteresis vanishes abruptly at $x_0$ (Fig.4). Note that we assume $B_{21} > 0$ and $B_{22} > 0$ but the sign “-” stands in (4) in front of $B_{21}$ and “+” precedes $B_{22}$. The alternative assumption, that there is a tricritical point at $(x_0, T_{A_i}(x))$, would imply a gradual disappearance of the thermal hysteresis as $x$ approaches $x_0$ from below.

Strong $x$-dependence of the thermal hysteresis at $x < x_0$ is unusual. From (5) it follows that $B_{21}$ increases with $x$ regardless of the sign of the electrostriction constant. At small $x$, this leads to a linear increase in $\Delta T_h(x)$ while at larger $x$, $\Delta T_h(x)$ increases quadratically, in excellent agreement with experiment (Fig.4).

From (7) it follows that the jump, $\Delta Q_1$, in AFE order parameter $Q_1$ should depend on the concentration $x$. Because $B_2$ increases linearly with $x$, so must $\Delta Q_1$. Experimentally, it is observed that as $x$ increases, so does the difference between the magnitudes of $\varepsilon'_m$ measured on cooling and on heating (Fig.1), which implies good agreement between theory and experiment.
Our data are insufficient to identify the crystal structure of the AFE phase associated with $Q_2=\text{finite}$ ($x_0 < x$) but some properties are clear: $\varepsilon'(T)$ is relaxor-like with a diffuse maximum and dispersion below $T_m$. Some properties however, are not typically relaxor-like: the dielectric permittivity magnitudes are much lower than those in typical relaxors such as PMN; the $\varepsilon'(T)$ fits the Curie-Weiss law well above $T_m$, but the extrapolated Curie-Weiss temperature, $T_{CW}$, is significantly below $T_m$ rather than above as in typical relaxors; in spite of the dramatic diffusion of $\varepsilon'(T)$, the frequency dependence of $\varepsilon'$ and $T_m$ is much weaker than in typical relaxors. The comparatively small magnitude of $\varepsilon'_m$ can be connected with the absence of the large contribution of lead to the dielectric permittivity.

IV SUMMARY

From the discussion above it follows that one of the main reasons for the appearance of the relaxor-like properties in the NaNbO$_3$-based solid solutions belonging to group II can be the appearance of the (random) local strain (with nonvanishing average magnitude) stemmed from the impurities. Due to the electrostriction effect this results in the decrease of the AFE critical temperature, increase of the thermal hysteresis width with $x$, and, finally, with the appearance of a new diffuse phase transition with weak dispersion of the dielectric permittivity. Large diffusion of the $\varepsilon'(T)$ maxima in some solid solution compositions with $x > x_0$ and the possibility of shifting $T_m$ to the room temperature range in conjunction with relatively weak frequency dependence of both $T_m$ and $\varepsilon'_m$ may be of certain interest for applications. The same is true for solid solution compositions with $x < x_0$ exhibiting giant $\varepsilon'(T)$ thermal hysteresis values.

V ACKNOWLEDGMENTS

This work was partially supported by Russian Foundation for Basic Research (Grants # 01-03-33119 and 01-02-16029). S.A.P. appreciates discussions with M. Glinchuk and B. Burton.

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