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Tunable Dielectric Characteristics of $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$

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Abstract. Tunable dielectric characteristics of $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ relaxor ferroelectric ceramics were investigated as the function of DC bias field and temperature. High tunability (more than 20%) was obtained in the present ceramics under a relatively weak DC bias field (1.4 kV/cm). The value of tunability changed from negative to positive with increasing DC field. For the simulation of the dielectric constant under DC bias field, modified model needs to be constructed for the relaxor ferroelectrics. The dielectric constant curve as a function of temperature without and under DC field was well fitted using the equation of diffuse phase transition. The lower $\varepsilon_{\max}$, higher $T_{\max}$ and higher diffuseness parameter under DC field were observed and only the lower $\varepsilon_{\max}$ contributed to positive tunability.

Keywords: relaxor, ferroelectric, tunability, DC field, complex perovskite

1. Introduction

Recently, the nonlinear nature of ferroelectrics has attracted much scientific and commercial attention because of its important applications in tunable microwave devices, such as voltage-controlled oscillators, tunable filters and phase shifters. A number of review papers have appeared recently, covering different aspects of tunable ferroelectric materials and their application [1, 2]. As candidates for microwave tunable materials, $(Ba,Sr)TiO_3$, $Cd_2Nb_2O_7$ and $K(Ta,Nb)O_3$ etc. are discussed by Tagantsev et al. [1]. However, the lead-based complex perovskite relaxor ferroelectrics have not received enough attention for the strong frequency dispersion which would induce high dielectric loss at microwave frequency [3, 4].

$Pb(Fe_{1/2}Nb_{1/2})O_3$ is an important member in the family of lead-based complex perovskites which is of interest as a component in commercial electronic ceramic materials for its high relative permittivity and low sintering temperature [5]. As an exception of relaxor ferroelectrics, $Pb(Fe_{1/2}Nb_{1/2})O_3$ shows a diffuse permittivity maximum but no frequency dispersion because of lack of long-range order [3]. Recently, in the author's work, good dielectric properties were obtained by incorporating the quantum paraelectric calcium titanate into lead iron niobate matrix [6]. At the rate composition of $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$, low loss ($10^{-3}$ order) dielectric is obtained with the high dielectric constant and its Curie temperature near room temperature.

For room temperature applications, ferroelectric materials such as (Ba, Sr)TiO_3, $Pb_xSr_{1-x}TiO_3$ and $Ba(Zr,Ti)O_3$ etc. [7–9], characterized by close values of Curie temperature near room temperature and diffuse phase transition, are well studied for tunable microwave applications. To further understand the tunable mechanism and develop other tunable materials, the tunable dielectric properties under DC bias field are investigated for $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ with characteristics similar to the above ferroelectric materials.

2. Experimental

$0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ ceramics were prepared by a solid-state reaction process with the columbite precursor method, where the raw powders all had high purity (more than 99%). $FeNbO_4$ powders were first synthesized at 1100°C in air for 3 h from Fe_2O_3 and Nb_2O_5, then

$0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ powders were synthesized by calcining the mixtures of $FeNbO_4$, PbO, $CaCO_3$, and TiO_2 at 850°C for 3 h. The synthesized powders were pressed into compacts of 12 mm in diameter under 98 MPa, and then sintered at 1000 to 1250°C in air for 3 h. The samples were polished to 0.25 mm thickness and silver paste was used as the electrodes.

The crystalline phases of the sintered samples were identified by the X-ray powder diffraction pattern using Cu K_α radiation. Polarization hysteresis loops were also examined by a hysteresis meter (RT-6000HVS) at room temperature. The temperature dependence of dielectric constant and the dielectric responses under DC bias voltage (0.6 kV/cm, 1 kV/cm, 1.4 kV/cm) were evaluated in the temperature range from −20°C to 100°C at 10 k–1 MHz by an LCR precise meter (HP4284A) equipped with a thermostat.

3. Discussion and Results

In the previous work, the cubic perovskite structure is identified through XRD analysis in $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$. However, the lower symmetry is indicated for the P-E hysteresis loops shown in Fig. 1. The slim hysteresis loops shown in Fig. 1 indicate the relaxor ferroelectric nature.

Figure 2 gives the temperature dependence of the tunability of $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ under various DC fields at different frequencies. The tunability is defined as follows.

$$\text{tunability} = \frac{\varepsilon_r(T,0) - \varepsilon_r(T,E)}{\varepsilon_r(T,0)} \times 100\% \qquad (1)$$

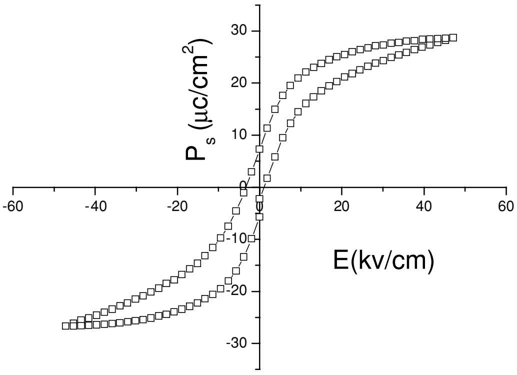

Fig. 1. E-P Hysteresis loop of $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ ceramics measured at 20°C.

As shown in Fig. 2, the maximum of tunability is higher than 20% under a relatively weak DC field of 1.4 kV/cm at 100 kHz and the tunability keeps on the order of 10% in a broad temperature range around room temperature. To explore explicit functional dependence of the dielectric constant in the paraelectric phase under the DC field, Johnson proposed an expression based on the framework of the phenomenological theory of Devonshire [10] as following:

$$\varepsilon_r = \frac{\varepsilon_r(T,0)}{\{1 + [\varepsilon_0 \varepsilon_r(T,0)]^3 B(T) E^2\}^{\frac{1}{3}}} \qquad (2)$$

where $\varepsilon_r(T, 0)$ and $B(T)$ is the initial dielectric constant under zero DC field and anharmonic coefficient, respectively. According to the above equation, a higher tunability is expected in the present material at a higher DC field.

It should be noted that the materials in ferroelectric state at low temperature shows opposite tunable characterization under different DC fields. Under a weak DC field, the value of tunability is negative, and the value of tunabiltiy changes from negative to positive with increasing DC field. This behavior is unexpected since it is considered that the application of a DC electric field results in a decrease in the dielectric constant for ferroelectrics. This behavior is known for 'antiferroelectric' behavior such as $(Na_{0.5}Bi_{0.5})TiO_3$-$SrTiO_3$ solutions [11] and $KNbO_3/KTaO_3$ superlattices [12]. In those cases, the increase in dielectric constant is due to antiferroelectric phase transforming to ferroelectric phase for the application of DC field. But there is no direct evidence for the existence of antiferroelectric in the present sample. The DC field for appearance of the negative tunability is very weak in the sample. Recently, the behavior of the increase in dielectric constant with weak DC field for ferroelectrics is also found in $BaSn_{0.1}Ti_{0.9}O_3$ (see Fig. 3 in ref. [13]). If ferroelectricity arises from soft phonon, it is easy to understand the positive tunability because application of DC field hardens the phonon mode and then dielectric constant decreases. For a virgin sample in the ferroelectric phase, the material is composed of domains which are randomly oriented so that a sample exhibits no net polarization. If only two dipoles orientations are assumed in one cell: one in the direction of the applied field and the other in the opposite direction. The dipole-dipole interaction in the opposite direction would be constrained by application of the weak DC field and it can be thought of the softness of the phonon

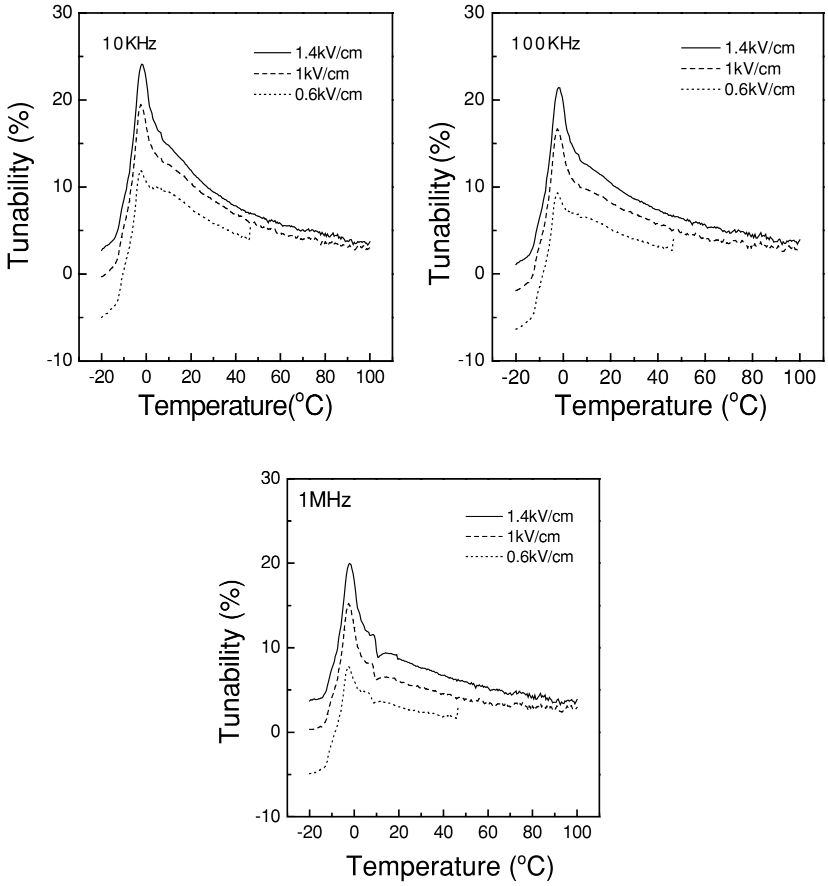

Fig. 2. Dielectric constant tunability as function of temperature at different DC bias field measured at different frequency for $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ ceramics.

mode in the opposite direction dipoles. This behavior is the origin of the negative tunability for the ferroelectric phase under weak DC field and it is easy to be ignored when seeking for the large positive tunability in the paraelectric phase. When DC field increases, dielectric constant increases first and then decreases and the behavior also corresponds to the slope (∂P/∂E) of the experimental and theory initial polarization curves in ferroelectric materials. The anhysteretic curve, initial curve and hysteresis loops in ferroeelctrics can be fit well using the domain wall model analogue to that in the ferromagnets [14, 15].

The phenomenological theory is not suitable to calculate the field dependence and the temperature dependence of dielectric constant in ferroelectrics in case of weak electric fields and the unknown temperature dependence of anharmonic coefficient. For the dielectric non-linearity at an arbitrary DC field, Vendik et al. has suggested a convenient form for calculation of the dependence of the permittivity under the DC bias field [16, 17]:

$$(\varepsilon_{\text{eff}})^{-1} = (\varepsilon_{00})^{-1}\{[(\zeta^2+\eta^3)^{1/2}+\xi]^{1/3} + [(\zeta^2+\eta^3)^{1/2}-\zeta]^{2/3}-\eta\}; \quad (3)$$

$$\zeta = [\zeta_S^2+\zeta_B^2]^{1/2}; \quad (4)$$

$$\zeta_S = (\theta_F/T_c)[1/16+(T_m/\theta_F)^2]^{1/2}-1; \quad (5)$$

$$\zeta_B = E_0/E_N; \quad (6)$$

$$\eta(T) = (\theta_F/T_c)[1/16+(T/\theta_F)^2]^{1/2}-1; \quad (7)$$

ε_{00} is the analog of the Curie constant; T_c is the Curie temperature of the materials; θ_F is the effective Debye

Table 1. Parameters of the Vendik's model for $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ and $Ba_{0.5}Sr_{0.5}TiO_3$ [17] ceramics.

Composition	T_c (K)	θ_F (K)	E_N (kv/cm)	ε_{00}	ξ_S
$Ba_{0.5}Sr_{0.5}TiO_3$	245	175	225	400	0.3
$0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$	266	189	26.5 (at DC field 0.6 kv/cm) 34.2 (at DC field 1 kv/cm) 41.3 (at DC field 1.4 kv/cm)	1516	0.045

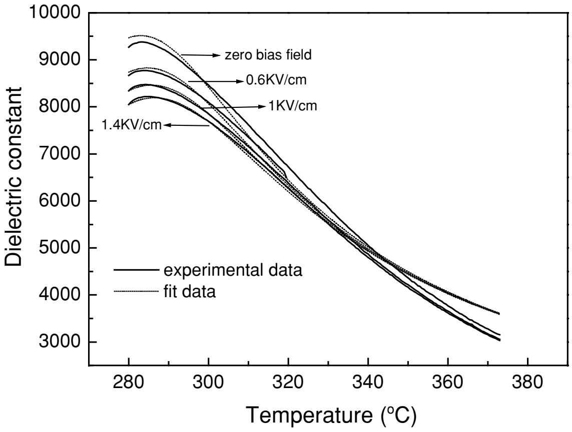

Fig. 3. Dependence of the $0.9Pb(Fe_{1/2}Nb_{1/2})O_3/0.1CaTiO_3$ dielectric constant (at 100 KHz) on temperature and DC field. The curves show the expermimental data and points are the simulation according to Eq. (3).

temperature; ξ_S is the statistical dispersion of the biasing field; E_N is the nomalizing field.

In this paper, we try to use the model to fit the present data except for the low temperature part where negative tunability may be appear. The model parameters for the sample are given in Table 1 and the fit results are shown in Fig. 3. Though some parameters are comparable to $Ba_{0.5}Sr_{0.5}TiO_3$, some unusual features are obtained. The model is not fit well with the experimental data under zero DC field especially for the high temperature part. Under different DC fields, experimental data cannot be fitted by using the constant E_N at the same time. For the aim of fitting experimental data under the different DC fields, the different E_N is used in Fig. 3 and the value is also shown in Table 1. Occasionally, E_0/E_N^2 is found to be a constant around 1/1200. If it is assumed that ξ_B equals to $E_0^{1/2}/E_N$, the value of 34.6 on E_N would be a good fit parameter. But the physical meaning is not clear. In summary, the model is not good for the present sample because the model was deduced from the dielectrics obey to the Curie-Weiss law but not for the relaxors. This indicates that the modified model is needed for the field dependence of dielectric constant in relaxor ferroelectrics.

To further understand the tunable mechanism in relaxor ferroelectrics, the experimental real part of dielectric constant ε versus T curves (at 100 kHz) under zero DC field and 1.4 kV/cm DC field are fitted using the following diffuse phase transition equation [18]:

$$\frac{1}{\varepsilon_r} = \frac{1}{\varepsilon_{\max}} + \left(\frac{T - T_{\max}}{\delta}\right)^2 \times \frac{1}{\varepsilon_{\max}} \tag{8}$$

where δ is the diffuseness parameter related to the peak broadening of the phase transition, $\varepsilon_{\max}$ is the maximum dielectric constant, and $T_{\max}$ is the temperature correspond to $\varepsilon_{\max}$. δ indicates the degree of the diffuse phase transition. The fitting and experimental values are shown in Fig. 4 and Table 2, and the lower $\varepsilon_{\max}$, higher $T_{\max}$ and diffuseness parameter under DC field have been observed. From Eq. (8), if two parameters are fixed, the qualitative contribution to the tunability can be obtained by changing the value of another parameter. Only the lower $\varepsilon_{\max}$ under DC field contributes to the positive tunability, and the higher $T_{\max}$ and diffuseness parameter have the opposite contribution. The lower $\varepsilon_{\max}$ and higher $T_{\max}$ under dc field can be deduced from the Eq. (3) in accordance with the Vendik's model for the normal ferroelectrics and the incipient ferroelectrics [17]. In lead-based complex perovskite relaxor ferroelectric, the diffuse characterization is always related to the order degree of B-site cation. The slightly increased δ value under DC field may be due to the reduced order degree in the present materials where the short-range order is observed through Raman analysis without DC field [6]. It is interesting to investigate the effect of DC field on cation ordering and the corresponding effect on the tunability in the future work.

Table 2. Experimental and fit parameters for 0.9Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$/0.1CaTiO$_3$.

	$\varepsilon_{\max}$ (exp)	$T_{\max}$ (exp)(°C)	$\varepsilon_{\max}$	$T_{\max}$(°C)	δ(°C)
0 kV/cm	9377	10	9521	2.99	48.2
1.4 kV/cm	8218	12	8286	7.31	49.6

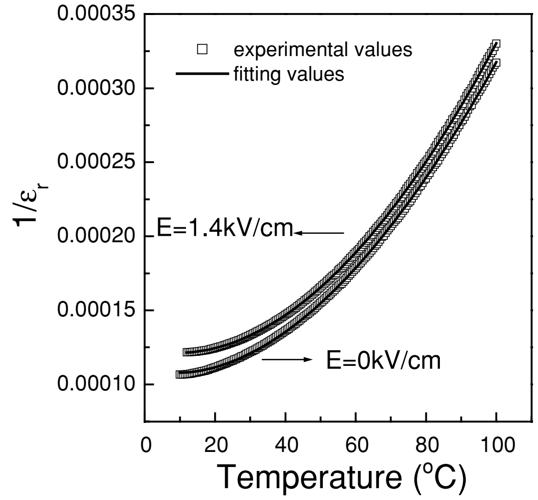

Fig. 4. Fitting and experimental values of $1/\varepsilon_r$ versus temperature for 0.9Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$/0.1CaTiO$_3$ ceramics.

4. Conclusions

The tunable dielectric characteristics of 0.9Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$/0.1CaTiO$_3$ were investigated in the present work. High tunability (more than 20%) was obtained under a relatively weak DC field (1.4 kV/cm). The value of tunability changed from negative to positive with increasing DC field. For the simulation of the dielectric constant under DC bias field, a modified model needs to be constructed for the relaxor ferroelectrics. Through fitting the dielectric constant curve as a function of temperature under zero and 1.4 kV/cm DC field, lower $\varepsilon_{\max}$, higher $T_{\max}$ and higher diffuseness parameter under DC field was observed and only the first contributed to positive tunability.

Modified Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ ceramics have great potential as tunable materials if the dielectric loss can be suppressed further and it is an interesting issue to investigate the effect of cation ordering on the tunability in future work.

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