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Nb_2O_5-based oxide ceramics and single crystals-investigation of dielectric properties

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Abstract

The behavior of enhancements of dielectric constant of Nb_2O_5 through small substituents of TiO_2 is of interest. The ceramics of these solid solutions were prepared by the conventional mixed oxide method. Single crystal fibers were grown by the Laser-Heated Pedestal Growth (LHPG) technique, which is considered to be a powerful tool for rapid growth of high-melting temperature oxides and incongruent melting compositions. The dielectric properties as function of temperature (−180 to 180 °C) and frequency (1 kHz to 1 MHz) were measured. The direct-current (dc) electric field dependence of the dielectric constant was also studied. The results show that a strong dielectric dispersion exists in a large frequency range, which implies that the relaxation process involved is not of a Debye-type. Relaxation dispersion was estimated by examining the influence of the cluster size distribution. The modified Devenshire relation including a cluster term was used to analyze data of dc bias field dependence of the dielectric constant, which gives the fitted parameters corresponding to cluster size distribution and their polar cluster polarization.

Keywords: C. Dielectric properties; D. TiO_2; Nb_2O_5

1. Introduction

There is a large volume of literature suggesting the existence of polar cluster nanoregions to describe the phenomena of strong frequency dispersion of the dielectric maxima in relaxor materials [1–5]. It is believed that a small variation in polar cluster size can lead to a wide dielectric dispersion covering several frequency decades. Thomas [2] has presented a theoretical framework for PMN in terms of the contributions made by individual NbO_6 and MgO_6 octahedra which he believed to be polar units. Bell [3] utilized a phenomenological approach to calculate the dielectric properties of relaxors using Cross's superparaelectric model [6]. Initially, relaxors were treated as (i) an ensemble of independent, identical, monosized superparaelectric clusters, and subsequently, (ii) a distribution in size of the clusters, (iii) temperature-dependent cluster size, and (iv) dipolar cluster interaction are supposed. The results from these scenarios suggested that a model involving a distribution of sizes and a temperature-dependent size gives the best qualitative fit to the relaxor behavior.

Quantum paraelectrics like $KTaO_3$ and $SrTiO_3$ are well known to undergo transitions into ferroelectric low temperature phases in the presence of small amount of polar impurities [7]. The polar clusters dispersed in a paraelectric matrix resembles, in many aspects, the superparamagnetic clusters in spin glasses. Consequently, Cross [6] suggested that the polar clusters are superparaelectric with the polarization vectors thermally fluctuating between equivalent potential wells. It has been proposed, in analogy with the cluster model of spin glasses that the polar clusters behave like large superparaelectric dipole moments. The broad distribution of relaxation times for cluster orientations originates from the distribution of the potential barriers separating different orientational state. The superparaelectric model based on the assumption of independent clusters cannot explain, however, the appearance of long-range order with the change of the material composition or due to an applied external field.

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This study tries to model quantitatively the dielectric response of relaxation in single crystal of Nb_2O_5-based solid solution which was assumed to be originated from the presence of small amounts of polar impurities. The polar impurities were treated as polar clusters. The influence of the cluster size dispersion is one assumption. Thus, the data of dc bias field dependence of the dielectric constant has been analyzed by the modified Devonshire relation including a cluster term giving the fitted parameters: cluster sizes distribution and their polar cluster polarization. The details of the approach are given in Section 3.

2. Experimental procedure

The experiments were performed on a single crystal sample of $Nb_2O_5(0.95)$:$TiO_2(0.05)$. Complex dielectric constant measurements were made using an automated measurement system. This system consisted of an LCR meter (HP 4284A) with the ac field of 1 V/mm. Measurements were made at temperatures between −180 and 180 °C at a rate of 2°/min.

Tunability measurements were conducted in the same system with the addition of a voltage source (TREK 610) and a high voltage blocking circuit that isolated the LCR meter from the high voltages applied to the sample. A dc voltage was applied to the sample. At each measuring temperature the sample was allowed to maintain thermal equilibrium for 15 min before the field dependence of the dielectric constant and loss data were recorded.

3. Results and discussion

3.1. Temperature dependence of the dielectric constant and loss

Temperature dependence of the dielectric constant (K) and dielectric loss ($\tan\delta$) as a function of frequency for $Nb_2O_5(0.95)$:$TiO_2(0.05)$ single crystal sample is shown in Fig. 1. From −180 to 180 °C, K increases continuously with sharp drop at temperature about 120 °C. This single crystal yields very high dielectric constant when compared to the conventional dielectric materials. However, there is a loss $\tan\delta$ peak with a frequency dispersive behavior. Two relaxation modes were clearly observed within the measurement temperature ranges. The analyses of relaxation mechanism were done in the previous chapter. The strong dispersion which exists in a large frequency range implies that the relaxation process involved is not a Debye-type.

3.2. Field dependence of the dielectric constant and loss

The dc electric field dependence of the K and $\tan\delta$ around the temperatures of dispersion range is illustrated in Fig. 2(a) and (b), respectively. It clearly shows that both K and $\tan\delta$ decrease with increasing electric field from 0 to 20 kV/cm. For example, at $T = 60$ °C, the dielectric maximum ($K = 352$) at 20 kV/cm is much lower than the value ($K = 871$) at zero electric field.

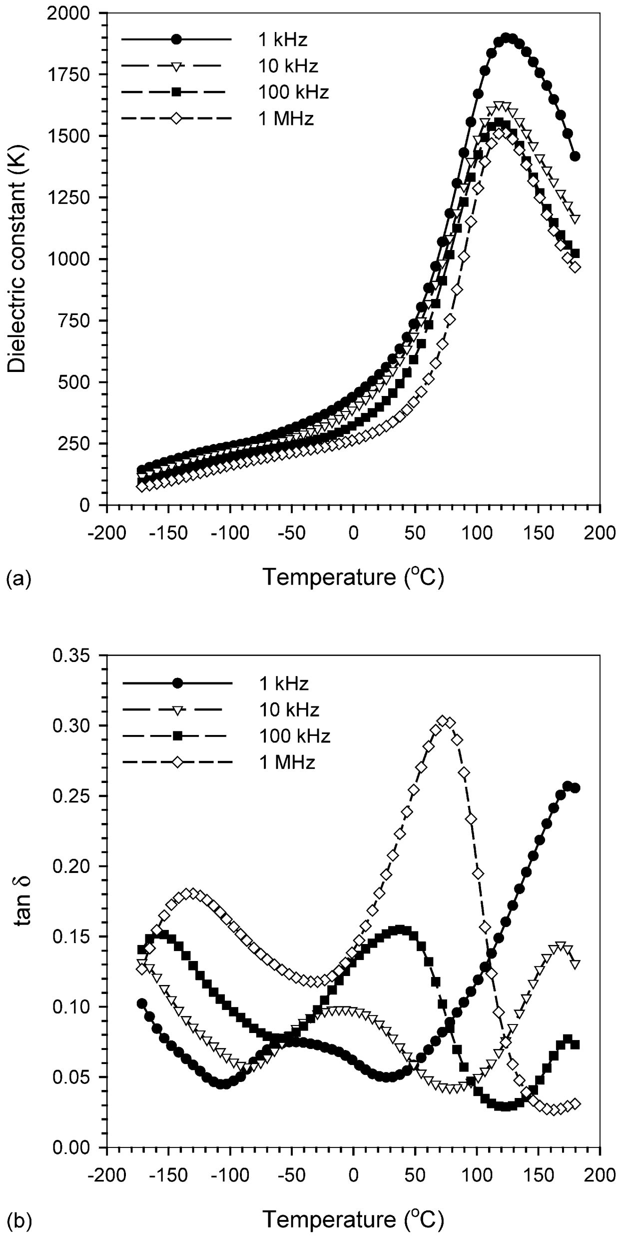

Fig. 1. Temperature dependence of dielectric constant (a) and dielectric loss (b) for $Nb_2O_5(0.95)$:$TiO_2(0.05)$ single crystal (perpendicular plane to the growth direction) at various frequencies.

The tunability is defined as the change in the dielectric constant under an applied electric field relative to the initial unbiased value, that is,

$$\text{Tunability}(\%) = \left(\frac{K(E_0) - K(E)}{K(E_0)}\right) \times 100\% \qquad (1)$$

where, $E_0 = 0$ kV/cm and E is the electric field at which we calculate the tunability. The bias field dependence of the tunability at various temperatures is shown in Fig. 3.

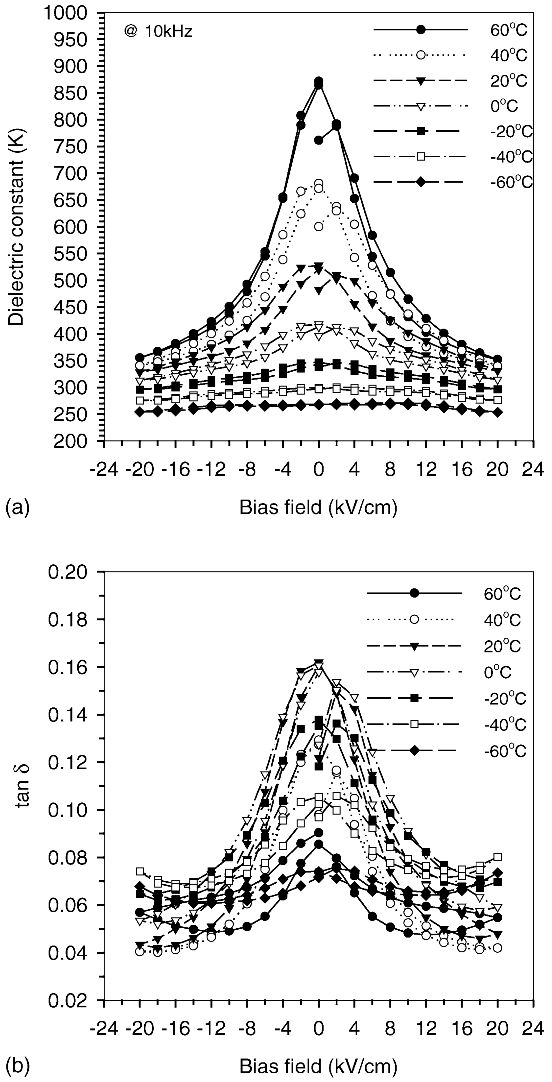

Fig. 2. Bias field dependence of dielectric constant (a) and dielectric loss (tan δ) (b) of $Nb_2O_5(0.95)$:$TiO_2(0.05)$ single crystal at 10 kHz.

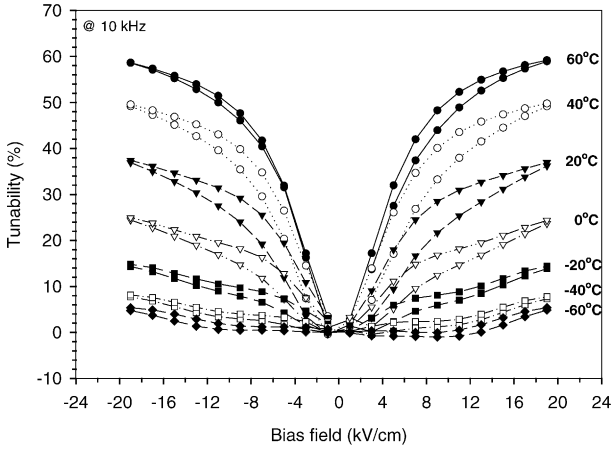

Fig. 3. Bias field dependence of the tunability (%) of $Nb_2O_5(0.95)$: $TiO_2(0.05)$ single crystal at 10 kHz.

At higher temperature, the tunability is higher than those of lower temperature. The high value of 59% tunability was obtained when the sample was applied an electric field of 20 kV/cm at 60 °C.

From the results, it was obvious that the polar clusters exist in this sample. As temperature was decreased, these polar clusters were possibly frozen (and some may coalesce to form the bigger size) that reduces the agility to respond to the external field.

3.3. *Fits to the modified Devonshire relation*

According to the Devonshire's thermodynamic theory, the dielectric behavior in a paraelectric state under low dc electric fields can be expressed as [8,9]:

$$\varepsilon(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4 \qquad (2)$$

where, ε_1 is the linear dielectric constant and $\varepsilon_{2,3}$ are the first and second nonlinear dielectric constant, respectively; and E is dc electric field. Eq. (2) has been widely adopted to analyze the electric field dependence of the dielectric behavior of nonlinear dielectrics [4,10,11]. However, the poor fits of $\varepsilon(E)$ versus E is not enough to explain the semibell-shaped curves in Figs. 4 and 5. The deviation from Eq. (2) implies that there is an excess contribution beyond the paraelectric matrix.

In addition to a background contribution coming from the intrinsic behavior, it was found that a polar cluster contribution-Langevin-type polar cluster contribution term has to be taken into account [4]. By means of the Langevin-type approach, the total polarization of a cluster system can be expressed as [3]:

$$P_c = P_r \tanh\left(\frac{P_r L^3 E}{2k_B T}\right) \qquad (3)$$

with the effective polarization of one cluster P_r, the cluster size L, the electric field E, and Boltzmann's constant k_B. By assuming one cluster gives contribution, $(1/\varepsilon_0)(\partial P_c/\partial E)$, at each electric field, therefore, the following equation is adopted to analyze the field dependence of dielectric constant:

$$\varepsilon(E) = \varepsilon_1 - \varepsilon_2 E^2 + \varepsilon_3 E^4 + \left[\frac{P_r \chi}{\varepsilon_0}\right][\cosh(E\chi)]^{-2} \qquad (4)$$

where, $\chi = (P_r L^3/2k_B T)$ with the cluster polarization P and diameters L, $\varepsilon_{1,2,3}$, and ε_0 designate the linear, nonlinear, and high-order dielectric constant and that of vacuum, respectively. The Langevin-type term of the right side in Eq. (4) describes the contribution from the possible polar clusters. The other terms of the right side of Eq. (4) describes background dielectric response, which might correspond to the electric field dependence of ε of the host lattice.

Eq. (4) was used to fit the electric field dependent K data at temperatures of 60, 40, 20, and 0 °C. It can be seen from Fig. 4 that the fitting curves (solid lines) are in good agreement with the experimental data. The obtained parameters

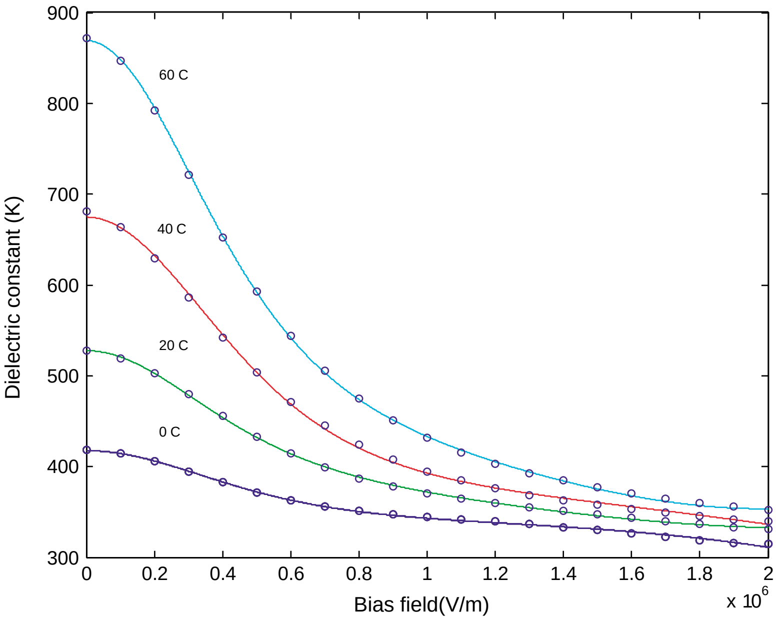

Fig. 4. Bias field dependence of dielectric constant K for $Nb_2O_5(0.95)$:$TiO_2(0.05)$ single crystal at 60, 40, 20, and 0 °C. The symbols: experimental data; the solid curves: the fit to Eq. (4).

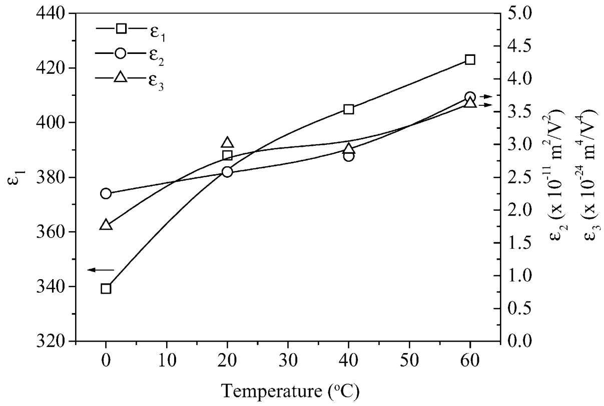

Fig. 5. Temperature dependence of the linear dielectric constant ε_1 and the nonlinear terms ε_2 and ε_3 obtained by the best fits of the dc electric field dependence of ε to Eq. (4).

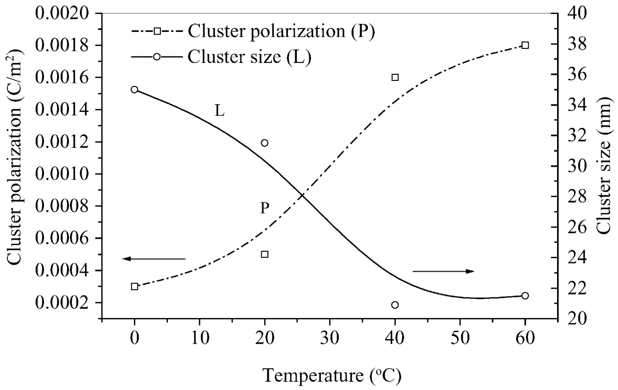

Fig. 6. Temperature dependence of the polar cluster polarization (P) and size (L) obtained by the best fits of the dc electric field dependence of ε to Eq. (4).

ε_1, ε_2, and ε_3 as a function of temperature are shown in Fig. 5. The size and polarization of the polar cluster obtained by fitting are shown in Fig. 6. The analysis shows that the size of polar cluster grows with decreasing temperature, whereas, the carried polarization is smaller with decreasing temperature. All parameters obtained from fitting curves are concluded in Table 1.

Table 1
Fitted parameter obtained from modified Devonshire relation

T (°C)	ε_1	ε_2 (m^2/V^2)	ε_3 (m^4/V^4)	P (C/m^2)	L (nm)
60	423	3.72×10^{-11}	3.62×10^{-24}	0.0018	21.5
40	404.89	2.82×10^{-11}	2.92×10^{-24}	0.0016	25.2
20	387.98	2.58×10^{-11}	3.01×10^{-24}	0.0005	31.5
0	339.22	2.25×10^{-11}	1.76×10^{-24}	0.0003	35.0

The type of polar clusters formed in this solid solution was believed to be generated from the existence of the Magneli phases, $Nb_2O_{5-\delta}$ [12] that were derived from reduction of Nb_2O_5. The obtained cluster sizes (L = 35–21.5 nm) was reasonable and in agreement with the lattice parameters of Magneli phases.

4. Summary

By applying dc electric field, significant suppression of K and $\tan\delta$ is observed. The electric field dependence of the dielectric constant can be well described by modified Devonshire relation including the cluster term. The polar clusters carry polarization P =~ 0.03–0.18 μC/cm^2 and the cluster size, L =~ 35–21.5 nm from 0 to 60 °C. This indicates that the relaxation probably results from the distributions of cluster polarizations and cluster sizes. This remark is consistent with the work of relaxor materials made by Viehland et al. [1]. It was shown that a small size variation can induce a dielectric dispersion covering several frequency decades. At this stage the conclusion for the exact type of polar cluster existed and their sizes in this sample cannot be reached, and the further investigation is needed.

References

[1] D. Viehland, S. Jang, L.E. Cross, M. Wuttig, J. Appl. Phys. 68 (1990) 2916.

[2] N.W. Thomas, J. Phys. Chem. Solids 51 (1990) 1419.

[3] A.J. Bell, J. Phys. Condens. Matter 5 (1993) 8773.

[4] U. Bianchi, J. Dec, W. Kleemann, J.G. Bednorz, Phys. Rev. B 51 (1995) 8737.

[5] Z.G. Lu, G. Calvarin, Phys. Rev. B 51 (1995) 2694.

[6] L.E. Cross, Ferroelectrics 76 (1987) 241.

[7] B.E. Vugmeister, M.D. Glinchuk, Rev. Mod. Phys. 62 (1990) 993.

[8] M.E. Lines, A.M. Glass, Principle and Application of Ferroelectrics and Related Materials, Oxford University Press, Oxford, 1977.

[9] A.F. Devonshire, Philos. Mag. 40 (1949) 1040.

[10] M.R. Chaves, A. Almeida, M. Maglione, J.L. Ribeiro, Phys. Status Solidi B 197 (1996) 503.

[11] C. Ang, L.E. Cross, R. Guo, A.S. Bhalla, Appl. Phys. Lett. 77 (2000) 732.

[12] R.J. Cava, B. Batlogg, J.J. Krajewski, H.F. Poulsen, P. Gammel, W.F. Peck Jr., L.W. Rupp Jr., Phys. Rev. B 44 (1991) 6973.