

Dielectric response of temperature-graded ferroelectric films

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The dielectric susceptibility and dielectric tunability of the temperature-graded BaTiO₃ thin films are investigated by using a modified transverse Ising model, taking the four-spin interaction and quantum fluctuation into account. There is a broad and smooth peak of the dielectric susceptibility at low temperature except for the sharp dielectric peak corresponding to the phase-transition temperature, irrespective of the sign of the temperature gradient. This behavior is different from the homogeneous bulk materials. Although the temperature gradient reduces the dielectric susceptibility, the temperature stability of the dielectric susceptibility can be effectively improved between the two dielectric peaks. The quantum fluctuation not only can enhance the temperature stability of the dielectric susceptibility but also has a significant influence on the dielectric tunability. Furthermore, a high dielectric tunability can be achieved by adjusting an appropriate positive temperature gradient, the quantum fluctuation strength, and the four-spin interaction strength. © 2005 American Institute of Physics. [DOI: 10.1063/1.2138369]

I. INTRODUCTION

Over the past few years, there has been considerable interest in polarization-graded ferroelectrics and their associated active structures: functionally graded ferroelectric devices (GFDs), a class of important functionally graded materials. These materials exhibit physical behaviors that cannot be observed in homogeneous bulk or thin-film ferroelectrics.¹⁻³ Such devices are usually formed from planar, capacitivelike structures by establishing a polarization gradient normal to the film surface, or equivalently in bulk materials, by their polarization gradient along the electric field normal to the electrodes when configured as capacitors. The most important features are the anomalous shift of hysteresis loop along the polarization axis (polarization offset) when the GFDs are placed in a modified Sawyer-Tower circuit and excited by an alternating electric field, as well as the large effective pyroelectric coefficient.⁴⁻⁶ Depending on the direction of hysteresis-loop shift, the graded structures are categorized into “up” (positive offset) and “down” (negative offset). The shifted hysteresis loops are attributed to “built-in” potentials, analogous to the asymmetric current-voltage characteristics resulting from the built-in potential across chemically doped regions in semiconductor diode junctions. Consequently, the graded structures have given rise to a particular class of transcapacitive ferroelectric devices, having potential applications in infrared detection, actuation, sensors, and energy storage devices.^{7,8} In addition, the attention on graded ferroelectric films has been recently renewed due to their excellent dielectric performance, such as a large di-

electric susceptibility, reasonably low dielectric loss, flatter susceptibility-temperature characteristic, and high dielectric tunability. These good dielectric properties enable them to be a class of promising candidate materials on microwave electronics applications, such as tunable filters, tunable oscillators, and phase shifters. Especially the dielectric tunability (i.e., the degree of variation in the dielectric susceptibility as a function of the applied electric field) is one of the key design parameters of tunable microwave devices.

It is well known that the spontaneous polarization of a ferroelectric sample is a function of material composition, temperature, and stress. Therefore, it enables the formation of GFDs from a variety of material systems, by chemically varying the composition, by imposing a temperature gradient normal to the electrode surfaces, and by imposing a stress gradient normal to their electrodes.^{9,10} Moreover, for the graded ferroelectric structures, the sign and degree of polarization offset observed from the experiments depend upon the direction and magnitude of the compositional gradient, the temperature gradient, and the stress gradient. Various compositionally graded ferroelectric films have been fabricated by different kinds of experimental techniques, including rf magnetron sputtering, sol gel, metal-organic chemical-vapor deposition, and laser ablation process. Prior experimental works on the functionally graded ferroelectric films have mainly focused on the origin of the abnormal polarization offset and dielectric properties of compositionally graded ferroelectric materials. Bao *et al.*¹¹ reported the dielectric enhancement and ferroelectric anomaly of compositionally graded (Pb,Ca)TiO₃ thin films. Lu *et al.*¹² found a high dielectric tunability in compositionally graded

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(Ba,Sr)TiO₃ films, which is higher than that of homogeneous (Ba,Sr)TiO₃ films. Cheng *et al.*¹³ demonstrated good temperature stability of dielectric susceptibility in the compositionally graded Ba_{0.80}Sr_{0.20}Ti_{1-x}Zr_xO₃ films. While there are extensive experimental results concerning compositionally graded ferroelectric structures, the description and theoretical analysis of the temperature-graded ferroelectric structures are still lacking. Only a few reports on the polarization offset and pyroelectric properties of the temperature-graded films can be found in the literature. Moreover, they paid little attention on the dielectric response of the temperature-graded films. In this work, we propose a modified transverse Ising model (TIM) to investigate the dielectric response of the temperature-graded ferroelectric films. It is expected that this theoretical analysis can shed light on the origin of anomalous polarization offsets in the temperature-graded ferroelectric thin films.

There are two theoretical approaches used to study ferroelectric properties: Ginzburg-Landau-Devonshire (GLD) phenomenological theory and the microscopic TIM. The generalized GLD model has been developed to study graded ferroic materials including ferroelectric, ferromagnetic, and ferroelastic materials.^{14,15} They are focused on the spatial inhomogeneities of polarization and the charge offset along the polarization axis of graded ferroelectric films, but the effect of temperature gradient on the dielectric properties has not been investigated by the GLD approach. On the other hand, the GLD theory is a macroscopic theory and is the continuum limit of the TIM,¹⁶ but it cannot tackle the quantum fluctuation effect. Investigations have shown that the quantum fluctuation has a very important influence on the structural and thermodynamic properties of the cubic perovskites. Zhong and Vanderbilt¹⁷ have studied the effects of quantum fluctuation on the structural phase transitions in SrTiO₃ and BaTiO₃. For BaTiO₃, they found that the quantum fluctuation reduced the transition temperature by 35–50 K. Wang *et al.*¹⁸ analyzed the phase-transition properties of temperature-graded ferroelectric films using the TIM, assuming a temperature-independent tunneling frequency and neglecting four-spin interaction. Since many ferroelectric materials, such as BaTiO₃, undergo first-order phase transitions, it is practical and interesting to introduce a four-spin exchange interaction term $J'_{ijkl}S_i^z S_j^z S_k^z S_l^z$ into the Hamiltonian of the TIM, which is analogous to a negative four-order polarization coefficient in the GLD theory and thus yields a first-order transition above a critical threshold. In our previous work, we have successfully applied the TIM including the quantum fluctuation effect and four-spin interaction to study the polarization offset and pyroelectric properties of temperature-graded film.¹⁹ However, the dielectric properties have not been investigated. Consequently, the aim of this work is to investigate the dielectric response of temperature-graded ferroelectric films on the basis of the modified TIM. We will explore the impact of temperature gradient, quantum fluctuation, and four-spin interaction strength on the dielectric susceptibility and the dielectric tunability of the temperature-graded ferroelectric films.

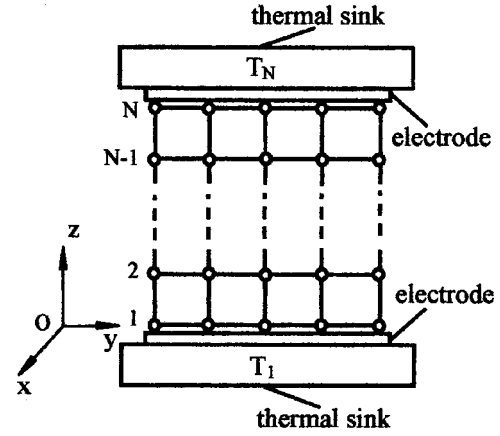


FIG. 1. Schematic illustration of the temperature-graded BaTiO₃ thin films with N layers. The z direction is perpendicular to the film surface.

II. FORMALISM

In this section, we develop a theoretical approach based on the TIM, taking the quantum fluctuation effect and four-spin exchange interaction into account, to analyze the dielectric susceptibility and the dielectric tunability of the temperature-graded BaTiO₃ thin films. The pseudospin approach under the TIM is generally believed to be a good microscopic description of perovskite-type ferroelectric materials, which has also been successfully applied to study the properties of the finite-size ferroelectrics, such as ferroelectric films and superlattice structures. A monodomain, single-crystal, temperature-graded BaTiO₃ thin film with N layers sandwiched between the two metallic electrodes is depicted in Fig. 1. The easy axis of polarization is along the z axis perpendicular to the film surface. Each layer is defined on the x - y plane and each pseudospin is located in the two-dimensional (2D) square lattice along the layer. The two electrodes are contact with thermal sinks at temperatures T_1 and T_N , imposing a temperature gradient across the BaTiO₃ film. It is assumed that a steady-state heat transfer is established, and the ferroelectric film is considered to be thermally homogeneous along the x and y directions. Accordingly, in the presence of four-spin interaction, the Hamiltonian of the graded film can be described by the TIM as

$$H = - \sum_{\langle ij \rangle} J_{ij} S_i^z S_j^z - \sum_{\langle ijkl \rangle} J'_{ijkl} S_i^z S_j^z S_k^z S_l^z - \sum_i \Omega_i S_i^x - 2\mu E \sum_i S_i^z, \quad (1)$$

where S_i^z and S_i^x denote the z and x components of a spin-1/2 operator at site i , $S_i^z = \pm 1/2$, J_{ij} the coupling coefficient between the nearest-neighbor sites i and j , J'_{ijkl} the four-spin interaction coefficient, Ω_i the tunneling frequency of site i , μ the effective dipole moment, and E the longitudinal external electric field. Considering that the environment of sites in the same layer as identical, we assume that the average value of the pseudospin in the same layer has the same value. Within the framework of the mean-field approximation, the average pseudospin along the z direction in the i th layer can be expressed as follows:¹⁹

$$R_i = \langle S_i^z \rangle = \frac{\langle H_i^z \rangle}{2|H_i|} \tanh \frac{|H_i|}{2k_B T_i}, \quad (2)$$

where

$$|H_i^z| = \sum_j J_{ij} \langle S_j^z \rangle + \sum_{jkl} J'_{ijkl} \langle S_j^z \rangle \langle S_k^z \rangle \langle S_l^z \rangle + 2\mu E, \quad (3)$$

$$|H_i| = \sqrt{\Omega_i^2 + (\langle H_i^z \rangle)^2}. \quad (4)$$

As the nearest-neighboring four-spin interactions are between four spins either in the same layer or in the two neighboring layers, the interaction coefficient J'_{ijkl} can be simplified as J'_{ij} , then we have

$$\begin{aligned} \langle H_i^z \rangle = & J_{i,i-1} R_{i-1} + 4J_{i,i} R_i + J_{i,i+1} R_{i+1} + 4J'_{i,i-1} R_i R_{i-1}^2 \\ & + 4J'_{i,i+1} R_i R_{i+1}^2 + 4J'_{i,i} R_i^3 + 2\mu E. \end{aligned} \quad (5)$$

For simplicity, we suppose that the temperature in the i th layer, T_i , linearly varies between the adjacent layers, and can be described by

$$T_i = T_1 + (i-1)\Delta T, \quad (6)$$

where ΔT is the temperature increment per layer which scales the magnitude of the temperature gradient, i runs over all the layers in the ferroelectric film, that is $i=1, 2, \dots, N$.

On the other hand, in order to consider the impact of quantum fluctuation on the graded films, the tunneling frequency can be written as²⁰

$$\Omega_i = g\Omega_{T_0} \left(1 - \frac{T_i}{391.0}\right) + \Omega_{T_0}, \quad (7)$$

where g is a parameter indicating the strength of quantum fluctuation and Ω_{T_0} is the tunneling frequency at the actual Curie-Weiss temperature T_0 (391.0 K) for BaTiO₃. Before this publication, the effect of quantum fluctuation on the dielectric properties of temperature-graded ferroelectric films has not been reported elsewhere. Equation (7) demonstrates that the tunneling frequency depends on the temperature of the specific layer and varies from layer to layer in the presence of the temperature gradient in the film. Zhong and Vanderbilt¹⁷ have proved that the quantum fluctuations increases with decreasing temperature. This suggests that the tunneling frequency will, on average, increase with decreasing temperature. According to Eq. (7), the tunneling frequency Ω_i of the i th layer will increase linearly from Ω_{T_0} to $(g+1)\Omega_{T_0}$ when the temperature decreases from 391.0 to 0 K. Thus, the $k_B T_i$ in Eq. (2) represents the contribution of the thermal fluctuation, and the tunneling frequency Ω_i represents the contribution of the quantum fluctuation. For BaTiO₃, an eight-site potential exists around the Ti ion. The height h of the potential barrier is finite. When $k_B T_i$ is higher than the height h , the tunneling effect does not exist, which means $\Omega_i=0$. For low temperature with $k_B T_i < h$, the tunneling effect exists, implying $\Omega_i > 0$.

Let $\alpha_i = 2|H_i| / \tanh[|H_i| / (2k_B T_i)]$, R_i satisfies the following equation:

$$\begin{aligned} 4J'_{i,i} R_i^3 + [(4J_{i,i} - \alpha_i) + 4J'_{i,i-1} R_{i-1}^2 + 4J'_{i,i+1} R_{i+1}^2] \\ \times R_i + J_{i,i-1} R_{i-1} + J_{i,i+1} R_{i+1} + 2\mu E = 0. \end{aligned} \quad (8)$$

The above equation stands for a set of nonlinear simultaneous equations from which R_i can be calculated numerically. When we apply a weak electric field along the z direction, the mean dielectric susceptibility of the graded film can be determined by numerical differential calculation

$$\langle \chi \rangle = \frac{1}{N} \sum_{i=1}^N \frac{\partial P_i}{\partial E} = \frac{1}{N} \sum_{i=1}^N 2n\mu \frac{\partial R_i}{\partial E}. \quad (9)$$

$\partial R_i / \partial E$ satisfies the following equation:

$$\begin{aligned} \frac{\partial R_i}{\partial E} = G_i \left[\frac{1}{\alpha_i} - \frac{1}{\alpha_i} \frac{\langle H_i^z \rangle^2}{|H_i|^2} \right. \\ \left. + \frac{\langle H_i^z \rangle^2}{2|H_i|^2} \frac{1}{2k_B T_i} \frac{1}{\cosh^2(|H_i|/2k_B T_i)} \right], \end{aligned} \quad (10)$$

where

$$\begin{aligned} G_i = & \frac{\partial \langle H_i^z \rangle}{\partial E} \\ = & (12J'_{i,i} R_i^2 + 4J_{i,i} + 4J'_{i,i-1} R_{i-1}^2 + 4J'_{i,i+1} R_{i+1}^2) \frac{\partial R_i}{\partial E} \\ & + \left(8J'_{i,i-1} R_{i-1} \frac{\partial R_{i-1}}{\partial E} + 8J'_{i,i+1} R_{i+1} \frac{\partial R_{i+1}}{\partial E} \right) \\ & \times R_i + J_{i,i-1} \frac{\partial R_{i-1}}{\partial E} + J_{i,i+1} \frac{\partial R_{i+1}}{\partial E}. \end{aligned} \quad (11)$$

Combining Eq. (10) with Eq. (8), $\partial R_i / \partial E$ can be calculated numerically. Correspondingly, we define the dielectric tunability Φ as the variation in the dielectric response with applied field

$$\Phi = \frac{\langle \chi(0) \rangle - \langle \chi(E) \rangle}{\langle \chi(0) \rangle} 100\%, \quad (12)$$

where $\langle \chi(0) \rangle$ and $\langle \chi(E) \rangle$ represent the dielectric susceptibility at zero and a certain E field, respectively.

III. NUMERICAL RESULTS AND DISCUSSION

In this section, we discuss the effect of temperature gradient, quantum fluctuation strength, and four-spin exchange interaction strength on the dielectric susceptibility, the electric-field tunability of the dielectric susceptibility in the temperature-graded BaTiO₃ thin films. According to the sign of the temperature gradient, the film with the top-layer temperature higher than the bottom-layer temperature ($T_N > T_1$) is called positive temperature-graded structure. The one with the opposite direction ($T_N < T_1$) is called negative temperature-graded structure. In our calculation, the total thickness of the graded structure is set as $N=20$. The values of the concerned parameters are chosen as follows:²⁰ the nearest-neighboring interaction parameter $J=277.8k_B$ and the tunneling frequency $\Omega_{T_0}=384.4k_B$. Since the properties of

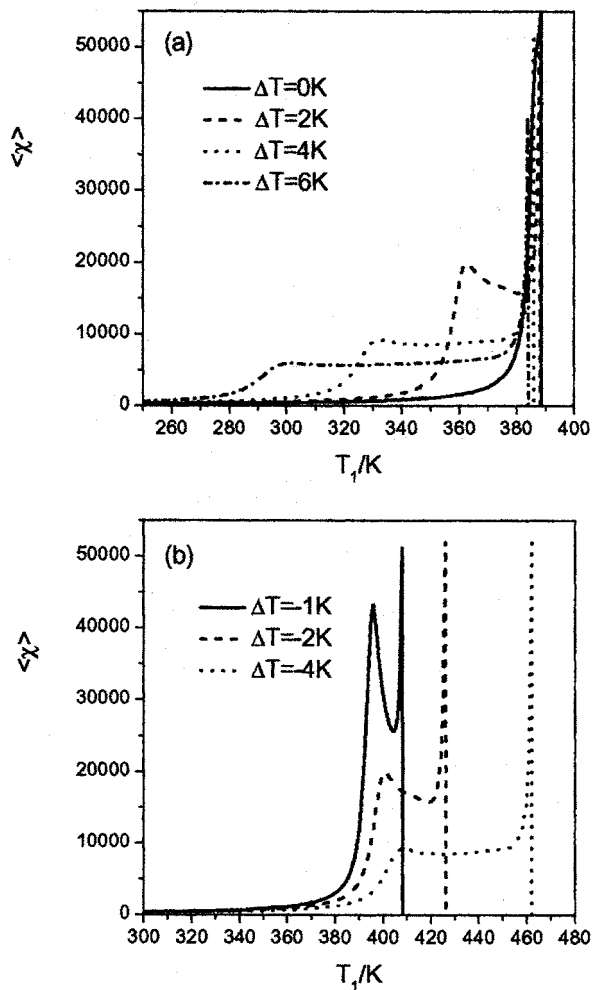


FIG. 2. The dependence of the mean dielectric susceptibility on the bottom-layer temperature T_1 in the absence of the external field for the different temperature gradients, given the quantum fluctuation parameter $g=1.0$ and the four-spin interaction parameter $J'=200.0k_B$, (a) and (b) corresponding to the cases of positive temperature gradient and negative temperature gradient, respectively.

the surface are different from those of the bulk, we take different parameters for the film surface: $J_s=1.45J$, $J'_s=1.45J'$, and $\Omega'_s=1.45\Omega$.

In Fig. 2, the dependence of the mean dielectric susceptibility on the bottom-layer temperature T_1 in the absence of the external field for the different temperature gradients is shown. The quantum fluctuation parameter is $g=1.0$ and the four-spin interaction parameter is $J'=200.0k_B$. (a) and (b) correspond to the cases of positive temperature gradient and negative temperature gradient, respectively. It can be clearly seen from Fig. 2(a) that the dielectric susceptibility exhibits the same feature as that of the bulk material without any temperature gradient ($\Delta T=0\text{K}$), and only one sharp peak occurs at the phase-transition temperature of the film. With the increase of the temperature gradient, the dielectric peak slightly shifts to lower temperature, which means that the phase-transition temperature decreases with the increase of the temperature gradient. It is interesting to note that for the temperature-graded ferroelectric film, there is a broad and smooth peak of the dielectric susceptibility at low temperature except for the sharp dielectric peak, which is similar to

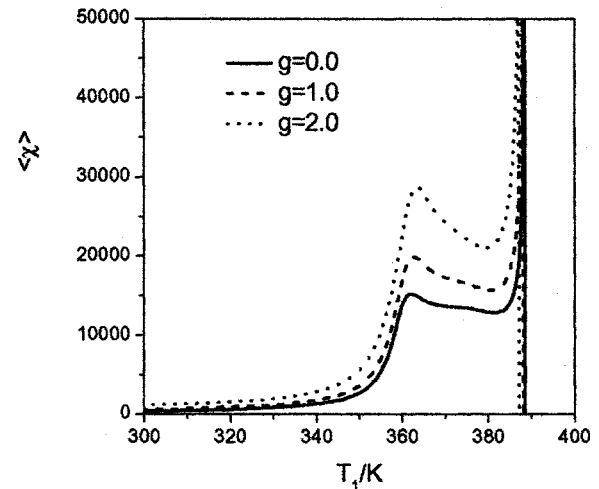


FIG. 3. The dielectric susceptibility as a function of the bottom-layer temperature T_1 in the absence of the external field for the different quantum fluctuation parameters ($g=0.0, 1.0, 2.0$), while the fixed four-spin interaction strength $J'=200.0k_B$.

the pyroelectric property of the temperature-graded ferroelectric film.¹⁹ Because of the temperature gradient, when some layers become disordered, the others are still in the ordered state, which will affect the polarization distribution and the dielectric response of the graded film. Besides, with the increase of temperature gradient, the smooth dielectric peak at low temperature not only becomes broader but also has a smaller value. For a large temperature gradient ($\Delta T=6\text{K}$), the temperature stability of dielectric susceptibility is enhanced by reducing the variation of dielectric susceptibility over a wide range of temperatures. This effect can be ascribed to the presence of the temperature gradient and satisfies the need of the tunable microwave devices. The realization of the temperature stability is a long-standing problem in high dielectric constant materials. Investigations have also revealed the coexistence of two or more phases, with both negative and positive temperature coefficients of susceptibility, respectively, can produce a material with good temperature stability of susceptibility. Therefore, temperature-graded ferroelectric films provide another effective means to achieve good temperature stability of dielectric susceptibility. For the negative temperature-graded ferroelectric films, as shown in Fig. 2(b), a sharp dielectric peak corresponding to the phase-transition temperature dramatically shifts to a higher temperature unlike the positive temperature gradient case. Although the dielectric susceptibility decreases with the increase of the temperature gradient, the temperature stability of dielectric susceptibility is significantly improved, similar to the compositional graded ferroelectric films. Experimental results showed that the temperature stability of susceptibility was improved by the increase of the gradients of compositions in the multilayer $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ films.¹³

Figure 3 displays the dielectric susceptibility as a function of the bottom-layer temperature T_1 in the absence of the external field for the different quantum fluctuation parameters ($g=0.0, 1.0, 2.0$), and at the fixed four-spin interaction strength $J'=200.0k_B$. It is obvious that for a given bottom-

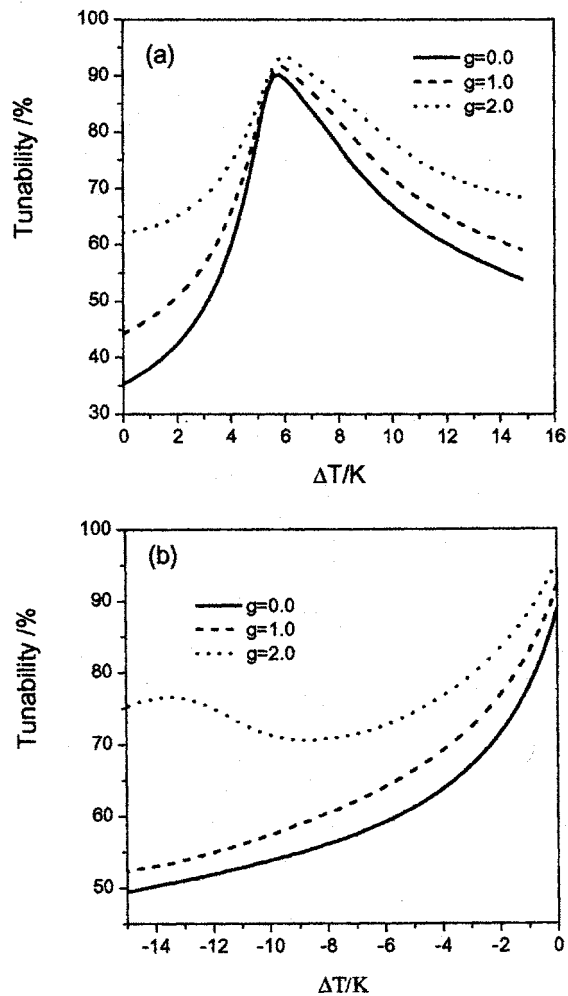


FIG. 4. The dielectric tunability as a function of the temperature gradient for the various quantum fluctuation parameters ($g=0.0, 1.0, 2.0$), (a) and (b) corresponding to the positive temperature gradient at a fixed $T_1=300$ K and the negative temperature gradient at a given $T_1=380$ K, respectively.

layer temperature, the dielectric susceptibility increases with the increase of the quantum fluctuation strength in the whole range of temperature. The quantum fluctuation makes the round dielectric peak at low temperature more obvious, but almost does not vary the position of the round dielectric peak. Thus, although the quantum fluctuation can enhance the dielectric susceptibility, there is no benefit to the temperature stability of dielectric susceptibility, especially between the two dielectric peaks. Besides, the temperature corresponding to the sharp peak of the dielectric susceptibility slightly shifts to lower temperature with the increase of the quantum fluctuation parameter.

In order to explore the impact of the temperature gradient on the dielectric tunability of the graded ferroelectric films, we calculate the dielectric tunability at dc electric field of 100 kV/cm, with a fixed bottom sink temperature T_1 and a varying top sink temperature T_N . The dielectric tunability as a function of the temperature gradient for the various quantum fluctuation parameters ($g=0.0, 1.0, 2.0$) is plotted in Figs. 4(a) and 4(b) corresponding to the positive temperature gradient at a fixed $T_1=300$ K and the negative temperature

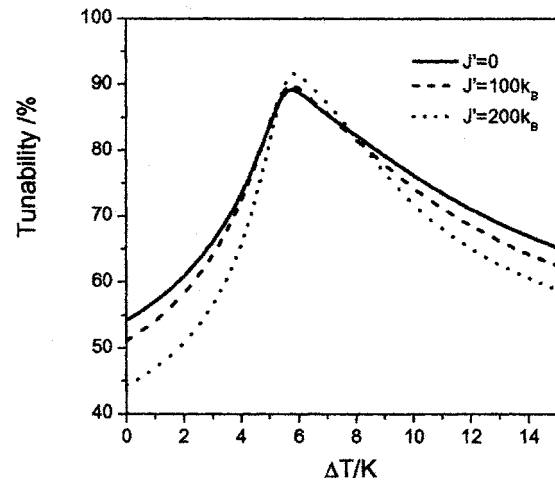


FIG. 5. The variation of the dielectric tunability as a function of the positive temperature gradient for different four-spin interaction parameters ($J'=0, J'=100.0k_B,$ and $J'=200.0k_B$), where the cold sink temperature is fixed at $T_1=300$ K.

gradient at a given $T_1=380$ K, respectively. As can be seen from Fig. 4(a), for a given quantum fluctuation strength, the dielectric tunability first increases in a continuous fashion with increasing the positive temperature gradient, reaching a maximum corresponding to a special temperature gradient, and then decreases with the further increase of the temperature gradient. For a given temperature gradient, the quantum fluctuation can effectively improve the dielectric tunability. In particular, the maximum of the dielectric tunability can reach 93.36% at a temperature gradient $\Delta T=6.0$ K and a fixed large quantum fluctuation strength $g=2.0$. Moreover, the impact of quantum fluctuation strength on the tunability is more pronounced at a temperature range away from the dielectric tunability peak. Compared with Fig. 4(a), the case of the negative temperature gradient displays the different phenomenon in Fig. 4(b). It is interesting to see that for a small given quantum fluctuation strength ($g=1.0$), the dielectric tunability decreases with the increase of the magnitude of the temperature gradient, but for a large quantum fluctuation strength ($g=2.0$), there is a round peak in the range of the large temperature gradient. This phenomenon can be attributed to the quantum fluctuation effect. With the increase of the magnitude of the temperature gradient, some layers close to the top electrode exist in the lower-temperature state, so the influence of quantum fluctuation on the dielectric response is enhanced. Furthermore, the quantum fluctuation can obviously improve the dielectric tunability while the magnitude of the negative temperature gradient is large enough. We can conclude that the high dielectric tunability can be obtained by adjusting an appropriate positive temperature gradient, but no similar effect can be obtained by negative temperature gradient. Besides, the dielectric tunability is not only electric-field independent, but also related to the temperature.

To better understand the four-spin interaction effect on the dielectric tunability, variation of the dielectric tunability as a function of the positive temperature gradient for different four-spin interaction parameters ($J'=0, J'=100.0k_B,$ and $J'=200.0k_B$) is depicted in Fig. 5, where the cold sink tem-

perature is fixed as $T_1=300$ K. We can easily observe that for a fixed four-spin interaction strength, the dielectric tunability first increases with the increase of the temperature gradient, and reaches the maximum at an appropriate temperature gradient, then decreases with the further increase of the temperature gradient. Close to the maximal dielectric tunability, the dielectric tunability increases with the increase of the four-spin interaction strength, otherwise the dielectric tunability decreases with an increase of the four-spin interaction.

IV. CONCLUSION

In summary, we have investigated the dielectric response of the temperature-graded BaTiO₃ thin films within the framework of the modified transverse Ising model, taking the four-spin interaction and quantum fluctuation into account. The effects of the temperature gradient, quantum fluctuation strength, and four-spin interaction on the dielectric susceptibility and the dielectric tunability are discussed. The calculated results reveal that there is a broad and smooth peak of the dielectric susceptibility at low temperature except a sharp dielectric peak corresponding to the phase-transition temperature, irrespective of the sign of the temperature gradient. This phenomenon is different from the homogeneous bulk materials and may have potential applications in designing the ferroelectric devices. Although the temperature gradient cannot increase the dielectric susceptibility, it can remarkably improve the temperature stability of the dielectric susceptibility, especially between the two dielectric peaks. Therefore, the temperature-graded ferroelectric films provide an effective means to acquire good temperature stability of dielectric susceptibility. The positive temperature gradient slightly shifts the sharp dielectric peak to a lower temperature, but the negative temperature gradient obviously shifts the peak in the other direction. In addition, for a given quantum fluctuation strength, the dielectric tunability has a maximum at a specific positive temperature gradient, which is different from the case of negative temperature gradient. Although the quantum fluctuation does not improve the temperature stability of dielectric susceptibility, it can remarkably increase the dielectric susceptibility. Besides, both the quantum fluctuation and the four-spin interaction can improve the maximum of the dielectric tunability. Therefore, a

high dielectric tunability can be achieved by adjusting an appropriate positive temperature gradient, the quantum fluctuation strength, and the four-spin interaction strength. From above we can conclude that both the quantum fluctuation and four-spin interaction should be taken into consideration when we investigate the thermodynamic properties of the temperature-graded ferroelectric films.

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