

Effect of electric field and post-treatment on dielectric behavior of SrTiO₃ single crystal

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The effect of dc electric field and post-treatment on the dielectric properties of SrTiO₃ single crystals are reported. Both the dielectric constant and the loss $\tan \delta$ decrease after post-treatment in flowing oxygen environment for 26 h at 1100 °C. The possible physical mechanism is briefly discussed. The dielectric behavior under dc electric field is measured. The rounded dielectric constant peak is induced by application of dc bias, and the corresponding dielectric loss is presented, which show more complicated behavior and usually are missing in the literature. In this work, it is found that the temperature (T_m) of the dielectric constant maximum shifts to higher temperatures with increasing dc electric field E , and follows the $T_m \sim E^{2/3}$ relation, indicating an induced ferroelectric-like behavior with the second-order phase transition under dc bias. © 2000 American Institute of Physics. [S0021-8979(00)03708-7]

I. INTRODUCTION

In order to meet the needs of continuously increasing developments in data processing and microwave communication, a series of microwave devices are being developed, such as frequency agile filters and tunable high- Q resonators. This demands a dielectric material with both high-electric-field tunability, $K = [\epsilon(E) - \epsilon(0)]/\epsilon(0)$, and very low dielectric loss at microwave frequency range. High tunability offers capability for broad-range adjustment of the working frequencies and low loss gives low noise, high selectivity, and compatibility with cryogenic electronics.¹⁻³

The quantum paraelectrics, SrTiO₃ and KTaO₃, have been recognized as promising candidate material, which show high-electric-field tunability at low temperatures along with reasonably low dielectric loss.³⁻⁶ However, it is also found that the dielectric quality of factor Q is deteriorated from more than an order of magnitude in SrTiO₃ thin films.⁶⁻⁸ Several factors, including nonstoichiometry, defects, high strain, and geometry effect in the thin film are the probable causes; however, a clear picture for the higher losses in thin-film SrTiO₃ has not been reached. In fact, the understanding of the dielectric loss under dc electric field for single crystal is also not clear so far.

In this article, we report the effect of dc electrical field and post-treatment on the dielectric properties of SrTiO₃ single crystals in an effort to obtain more experimental data to understand the dielectric behavior, especially, the loss mechanisms in SrTiO₃ and the electric-field effect.

II. EXPERIMENTAL PROCEDURE

Single-crystal samples with polished surface (100) were obtained from a commercial source. The samples were annealed in the furnace at 1100 °C for 26 h. The crystals were evaluated initially in the low-frequency range.

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Complex dielectric permittivity was measured using HP 4284A LCR meters in the frequency range 20 Hz–1 MHz with an ac field of 1 V/mm. The temperature dependence of the dielectric properties was measured in a cryostat system in the temperature range 12–300 K, while the specimen was being cooled or heated up at a cooling/heating rate of 1 K per minute, and readings were taken at every 1 or 2 K intervals.

The dc voltage was applied to the samples and a blocking circuit was adopted to separate the high-dc voltage and LCR meters. At each measuring temperature, the sample was allowed to reach thermal equilibration before the field dependence of the dielectric constant and loss measurement.

III. RESULTS AND DISCUSSION

A. Effect of the thermal treatment on the dielectric behavior

The temperature (T) dependencies of the dielectric constant (ϵ) and dielectric loss ($\tan \delta$) as a function of frequency for the as-grown SrTiO₃ sample are shown in Fig. 1. From 300 to 12 K, ϵ increases continuously with decreasing temperature and attained the value $\epsilon = 10\,300$ at 12 K. However, for $\tan \delta$, in the temperature range 50–100 K, there is a set of peaks with a frequency-dispersive behavior. With further decreasing temperature, as $T < 50$ K, the $\tan \delta$ increases sharply and ϵ increases correspondingly.

Similar $\tan \delta$ peaks were also observed in single crystals by Mizaras and Loidl,⁹ Viana *et al.*,¹⁰ in polycrystalline samples by some of the authors,^{11,12} and in thin films by Li *et al.*¹³

The relaxation rate for the polarization derived from the temperature dependence of the imaginary part of the permittivity for the sample is plotted in Fig. 2. The data were fitted to the Arrhenius relation

$$\nu = \nu_0 \exp[U/T], \quad (1)$$

where ν_0 is the relaxation rate at infinite temperature, U the activation energy for relaxation, and T the temperature. The

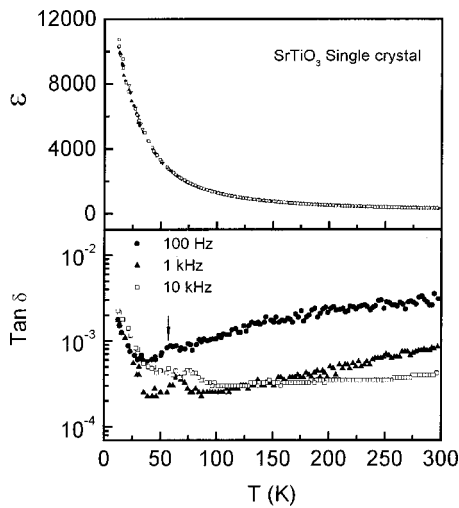


FIG. 1. Temperature dependence of ϵ and $\tan \delta$ as functions of frequencies for the as-grown SrTiO_3 single crystal.

fit parameters are $U=1222$ K and $\nu_0 \sim 10^{11}$ Hz. The activation energy $U=1222$ K is in good agreement with the parameter reported by Mizaras and Liodl.⁹

The dielectric properties of the samples, after annealing in flowing oxygen environment for 26 h, were measured. For comparison, the ϵ and $\tan \delta$ vs T plots at 10 kHz before and after annealing are shown in Fig. 3. It clearly shows that the dielectric constant and loss decrease after annealing the samples in oxygen atmosphere. The activation energy for the relaxation process for the sample before and after annealing is the same within the experimental error.

The relaxation process observed has been explained in terms of the dynamics of the domain walls that occur at the cubic-to-tetragonal phase transition.⁹ In general, the annealing in O_2 will eliminate fully or partially the internal stress and oxygen vacancies. If the dynamic response of the domain walls is solely responsible for the dielectric relaxation, the decrease in the internal stress and the oxygen vacancies would have led to an enhancement of the dielectric constant and the loss, as Robels, Schneider, and Arlt¹⁴ reported that oxygen vacancies can pin the motion of domain walls, and internal stresses can reduce the contribution of the domain boundary.

However, in this work, the experimental results show that both the dielectric constant and loss decrease after annealing in O_2 , which indicates that an alternative explanation is needed. It is well known that SrTiO_3 is a typical soft-mode

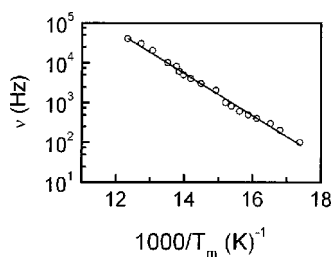


FIG. 2. Temperature dependence of the relaxation rate for the SrTiO_3 single crystal.

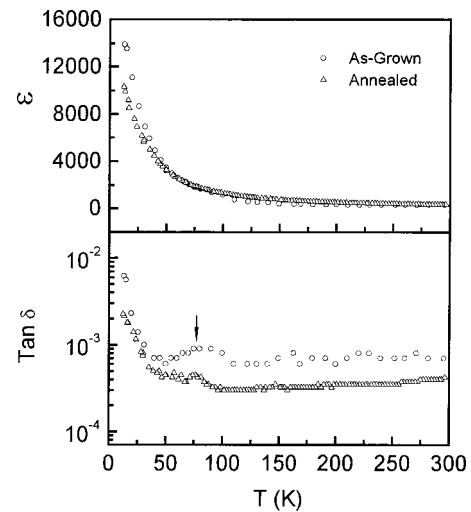


FIG. 3. Temperature dependences of ϵ and $\tan \delta$ at 10 kHz for the SrTiO_3 single crystal before and after annealing in the flowing oxygen atmosphere.

quantum paraelectric. In nominally pure SrTiO_3 , there exist low levels of unavoidable defects or impurities (for example, oxygen vacancies), therefore, it is highly possible that such defects could interact with the soft mode at low temperatures, and contribute to dielectric relaxations. Indeed, in the soft-mode quantum paraelectric KTaO_3 , the dielectric relaxation below 110 K was found to relate to the unavoidable defects/impurities.^{15,16} In SrTiO_3 doped with a small amount of Bi (500 ppm),¹² obvious enhancement of the similar relaxation process supports this conjecture. In this work, it is expected that, after annealing in O_2 , the densities of the oxygen vacancies were decreased, and the interaction between the oxygen vacancies and the soft mode decreased, hence, the dielectric constant and loss decreased. A clear understanding needs further work.

B. Effect of the electrical field on the dielectric behavior

Although the dc electric-field dependence of the dielectric properties in SrTiO_3 single crystals has been studied by several groups,^{17–22} dielectric loss data at low temperatures, especially under dc electric field, are rarely reported. In this work, we measured the temperature dependence of both the dielectric constant and loss under different dc fields (0–20 kV/cm), as shown in Figs. 4(a) and 4(b). The results show that a dielectric peak is induced by applying the dc electric field, this is a coincidence with those widely reported in the earlier literature.^{17–21} For the dielectric loss, the curve shows a more complicated behavior. In the temperature range of 12–120 K, at least three peaks under dc electric field can be identified. For example, at 4 kV/cm and 10 kHz, there are three peaks, peak A around 28 K, peak B around 50 K, and peak C around 75 K. As a preliminary discussion, peak A may correspond to the peak in the dielectric constant induced by the dc electric field and/or a defect mode; peak C is observed even for zero-electric field, which has been discussed in Sec. III A; peak B seems to relate to some defect mode. In

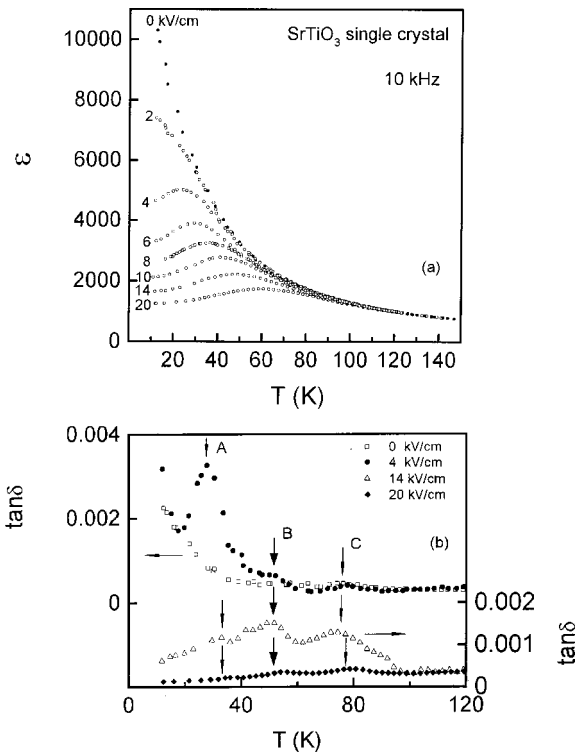


FIG. 4. Temperature dependence of (a) ϵ and (b) $\tan \delta$ at 10 kHz under different dc fields. For $\tan \delta$, only typical curves at several fields are shown in order to make the figure distinguishable.

this stage, the physical mechanism of the dielectric loss is still not clear, and further work is being conducted.

From Fig. 4(a), it can also be noted that the temperature (T_m) of the maximum of the dielectric constant increase with increasing dc electric field. It is known that for a normal ferroelectric with a second-order phase transition, the relation between T_c and the applied dc field follows as²³

$$T_c \sim E^{2/3}. \tag{2}$$

In the present work, we plot the field effect on T_m below 20 kV/cm assuming $T_m = T_c$. As shown in Fig. 5(a), the experimental data fit well to the predication of the theory. In a recent work, Fuchs *et al.*²⁴ reported the T_c vs E relation in thin film of SrTiO₃ and that it is not possible to distinguish whether the relation of T_c vs E follows $T_c \sim E^{2/3}$ or $T_c \sim E$. Comparing Figs. 5(a) and 5(b), it can be clearly seen that the relation between T_c and the applied dc field follows $T_c \sim E^{2/3}$ in SrTiO₃ bulk single crystal. This result implies that upon application of the dc electric field, the SrTiO₃ crystal behaves similar to a ferroelectric with a second-order phase transition.

It can be seen from Fig. 4(a) that at a fixed temperature, with increasing dc electric field, the dielectric constant is significantly suppressed. For example, at 12 K and 10 kHz, the dielectric constant was suppressed from 10 300 to 1240 while the dc electric field increased from 0 to 20 kV/cm. The tunability (K) of the dielectric constant of SrTiO₃ was calculated by using the expression

$$K = [\epsilon(0) - \epsilon(E)] / \epsilon(0). \tag{3}$$

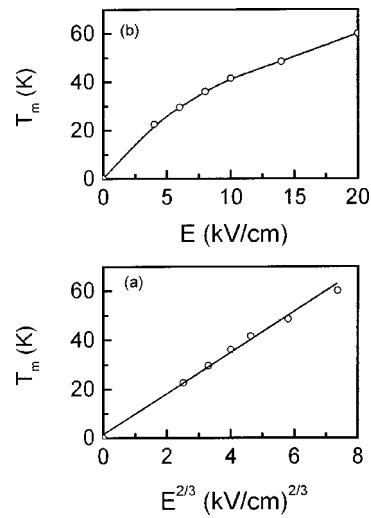


FIG. 5. (a) Plot of the T_m vs $E^{2/3}$; (b) plot of the T_m vs E .

High tunability 0.88 was obtained at 12 K for a dc electric field of 20 kV/cm. The temperature dependence of the tunability (K) at 20 kV/cm is shown in Fig. 6(a). Obviously, the tunability is also field dependent, as shown in Fig. 6(b).

IV. CONCLUSION

In conclusion, the effect of the dc electric field and post-thermal treatment on the dielectric properties of SrTiO₃ was studied. After post-treatment in flowing oxygen, the dielectric constant and loss decrease. A tentative explanation is suggested, i.e., in nominally pure or impurity-doped SrTiO₃ at low temperatures, the unavoidable defects or impurities (here, for example, oxygen vacancies) probably interact with the soft mode, and contribute to the dielectric relaxation. After annealing in O₂, the oxygen vacancies and internal stress were decreased, hence the dielectric constant and loss decreased.

Under dc electric field, the dielectric constant peak is induced, and the dielectric loss show several peaks. The field

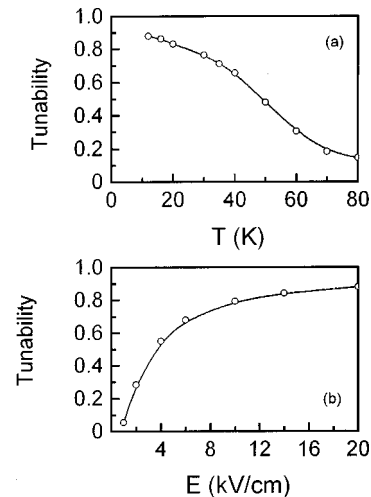


FIG. 6. (a) Temperature dependence of the dielectric tunability at 20 kV/cm and 10 kHz; (b) field dependence of the dielectric tunability at 12 K and 10 kHz.

dependence of the temperature of the dielectric constant maximum follows the $T_c \sim E^{2/3}$ relation, indicating a ferroelectric-like behavior with a second-order phase transition. At 20 kV/cm, 12 K, and 10 kHz, SrTiO₃ shows a very high dielectric tunability, $\approx 88\%$.

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