

Soft mode behavior in transition metal doped SrTiO₃ thin films on MgO substrates

A. V. Melentev^{a1)}, E. S. Zhukova^a, B. M. Nekrasov^a, V. S. Stolyarov^{a,b,c}, A. S. Frolov^a, M. Savinov^d, A. A. Bush^e,
V. I. Kozlov^{e,f}, B. P. Gorshunov^a, M. V. Talanov^a

^aMoscow Institute of Physics and Technology, 141700 Dolgoprudny, Russia

^bDukhov Research Institute of Automatics (VNIIA), 127055 Moscow, Russia

^cNational University of Science and Technology MISIS, 119049 Moscow, Russia

^dInstitute of Physics of the Czech Academy of Sciences, 18221 Prague, Czech Republic

^eResearch Institute of Solid-State Electronics Materials, MIREA – Russian Technological University (RTU MIREA),
119454 Moscow, Russia

^fKapitza Institute for Physical Problems of the Russian Academy of Sciences, 119334 Moscow, Russia

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The ferroelectric soft mode in polycrystalline pristine SrTiO₃ and weakly doped SrTiO₃:M (M = 2 at % Fe, Ni, Mn, Co) thin films on (001) MgO substrates has been studied using time-domain terahertz spectroscopy. Spectra of real and imaginary parts of film permittivity were determined in the frequency range of 5–100 cm⁻¹ at temperatures between 5 and 300 K. Central frequency and dielectric contribution of the ferroelectric soft mode show Barrett-like temperature dependencies similar to crystalline SrTiO₃. Large negative values of Curie temperature and enhanced positive values of Barrett quantum temperatures are discovered indicating that doped SrTiO₃ thin films are farther from ferroelectric phase transition than SrTiO₃ crystals.

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Strontium titanate (SrTiO₃, STO) is an archetypal quantum paraelectric with dielectric permittivity reaching values as high as 24000 at 4 K. It has found applications as a material for capacitors, actuators, sensors, memory devices and other electronic and microwave components. More than 95 % of the low-frequency dielectric permittivity in STO single crystals is associated with the ferroelectric soft mode (TO₁ mode, Slater mode). The temperature dependence of the soft mode dielectric contribution $\Delta\epsilon$ follows the Curie–Weiss behavior down to temperature ≈ 50 K, below which it levels off indicating suppression of the phase transition. This behavior was ascribed to quantum fluctuations by Barrett [1]. In addition to the Curie temperature T_C , Barrett's model introduces another parameter T_1 , which is related to the temperature below which quantum fluctuations become essential in determining physical properties of the compound.

Thin films of STO tend to have smaller $\Delta\epsilon$ and higher loss tangent than the bulk samples [2–4]. The same holds for polycrystalline samples compared to sin-

gle crystals. The low frequency $\Delta\epsilon$ of epitaxial films with high degree of crystallinity can reach values of $\approx 10^4$, while the $\Delta\epsilon$ of bulk ceramics or thin polycrystalline films can drop down to $\approx 10^3$ or even lower, depending on microstructure and synthesis procedure. STO polycrystalline thin films combine some of the valuable dielectric properties inherent in STO with low manufacturing cost, compatibility with planar fabrication processes and a variety of suitable substrates. There are several simple ways of tweaking the characteristics of thin films, e.g., using different substrates (misfit strain), changing grain size or chemical substitution. Misfit strain is more applicable to epitaxial films, and the influence of different grain size on the properties of polycrystalline films has been extensively studied in the literature, see, e.g. [3]. Chemical substitution as low as a few atomic percent has a noticeable impact on soft mode dynamics in bulk samples [5–10]. However, the majority of studies consider only radiofrequency dielectric properties, which are important for some applications, but not always representative of the changes in lattice dynamics induced by doping. Contactless tera-

¹⁾e-mail: aleksandr.melentyev@phystech.edu

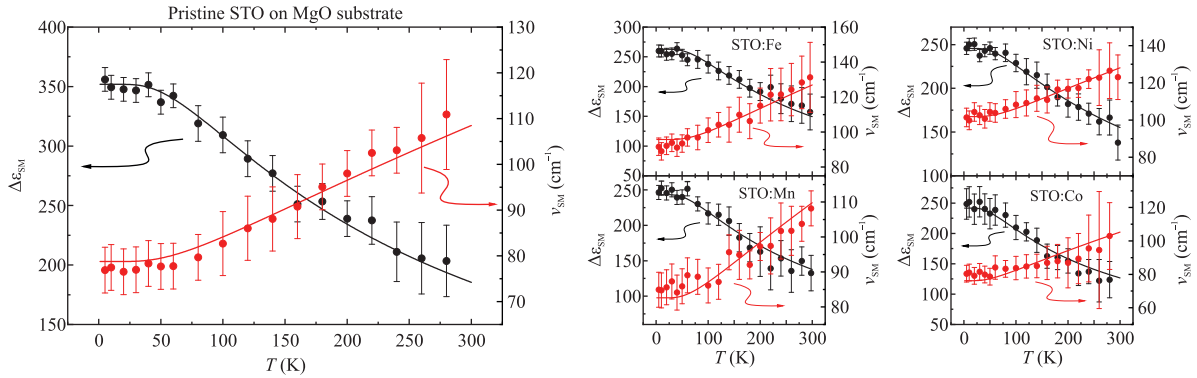


Fig. 1. (Color online) Temperature dependent soft mode frequency ν_{SM} and dielectric contribution $\Delta\epsilon_{SM}$ of pristine and M-doped STO thin films (M = Fe, Ni, Mn, Co) on MgO substrates. Dots represent experimental data, obtained from least-square fits of measured ϵ' , ϵ'' spectra. Solid lines represent least-square fit results with Barrett expressions (1), (2)

hertz spectroscopic methods are able to determine intrinsic properties of STO films without contribution of the parasitic effects like depletion layers, and to separate dielectric contribution of the TO_1 soft mode from all other excitations. In the present study, we have used time-domain terahertz (TDS-THz) spectroscopy which allows for the determination of the soft mode parameters (eigenfrequency, dielectric contribution, damping constant) on a quantitative level. We discover that transition metal doping drives STO films farther from the ferroelectric phase transition, which manifests itself as large in absolute values and negative Curie temperature in the Barrett expression. In addition, we find that the soft mode dielectric contribution at 4 K has the same value of ≈ 250 for different substituent cations.

The temperature dependencies of the soft mode parameters for all four studied films are presented in Fig. 1. The dielectric contribution $\Delta\epsilon_{SM}$ is two orders of magnitude lower than in undoped STO crystals, while the soft mode frequency ν_{SM} is higher than in STO crystals at all temperatures. Temperature-driven mode softening is less pronounced in thin films than in crystals; in crystals the ν_{SM} value changes by a factor of ≈ 10 between 300 and 5 K [11]. Despite the apparent differences in the values of the soft mode parameters in crystals and in our films, the behavior is qualitatively similar. The dielectric contribution grows with cooling and levels off below 60 K, and the frequency decreases and levels off below $\approx 100 \text{ cm}^{-1}$ (80 cm^{-1} for STO:Co). According to the Barrett formalism, such behavior is explained by quantum fluctuations suppressing the ferroelectric phase transition with the soft mode dielectric contribution and frequency given as:

$$\Delta\epsilon_{SM}(T) = \frac{C}{\left(\frac{T_1}{2}\right) \coth\left(\frac{T_1}{2T}\right) - T_C}, \quad (1)$$

$$\nu_{SM}(T) = \sqrt{D \left(\left(\frac{T_1}{2}\right) \coth\left(\frac{T_1}{2T}\right) - T_C \right)}. \quad (2)$$

Here C and T_C are the Curie constant and the Curie temperature, respectively, D is the Cochran constant and T_1 characterizes the energy of quantum fluctuations. The results of the simultaneous least-square processing of $\Delta\epsilon_{SM}(T)$ and $\nu_{SM}(T)$ dependencies with Barrett expressions (1), (2) are presented in Fig. 1 by solid lines.

Table 1. Soft mode parameters of STO:M thin films on MgO substrates derived from the least-square fits of experimental dependences $\Delta\epsilon_{SM}(T)$ and $\nu_{SM}(T)$ with the Barrett expressions (1), (2)

	T_1 , K	T_C , K	$C \times 10^{-3}$, K	D , $\text{cm}^{-2} \text{K}^{-1}$
STO	190 ± 20	-150 ± 50	85 ± 5	26 ± 3
STO:Fe	225 ± 20	-150 ± 60	70 ± 7	34 ± 3
STO:Ni	200 ± 30	-260 ± 80	89 ± 7	28 ± 3
STO:Mn	200 ± 20	-150 ± 60	66 ± 5	25 ± 3
STO:Co	150 ± 20	-180 ± 80	62 ± 5	23 ± 3

It is seen that all doped films have the same values of low temperature dielectric contribution, $\Delta\epsilon = 250 \pm 10$, within experimental uncertainties, independent on impurity ion. Pristine STO film, however, has noticeably higher $\Delta\epsilon = 350 \pm 10$, which is close to the values reported for pristine STO films deposited on (001) MgO under slightly different conditions with the same technique [12]. We note that for similarly doped polycrystalline STO films on (0001) oriented sapphire substrates, the dielectric contribution of the soft mode was somewhat smaller and varied from 150 for STO:Co to 200 for STO:Ni [13]. However, on both substrates, Al_2O_3 and MgO, doping resulted in a decrease in permittivity

and a hardening of the soft mode. Differences in microstructure and local strains are major factors, which can lead to the observed difference in dielectric properties. For example, smaller grain size leads to formation of polar nanoregions and larger role of the dead layers [3, 13]. The choice of substrate can influence both of these factors. On the one hand, due to the mismatch between the thermal expansion coefficients of the substrates ($7.5 \times 10^{-6} \text{ K}^{-1}$ for sapphire, $12.8 \times 10^{-6} \text{ K}^{-1}$ for MgO) and STO ($10.4 \times 10^{-6} \text{ K}^{-1}$), a thermal strain builds up in the films during cooling from the high deposition temperature of 973 K. This strain is biaxial in-plane tensile in STO on sapphire and compressive in STO on MgO. On the other hand, the microstructure of the films also depends on the substrate.

Table 1 features the Barrett parameters obtained for all studied films. The Curie constants are almost twice bigger in the films on MgO than in films on sapphire, approaching the value of the single crystalline STO [13]. The Curie temperature varies from -150 K (STO:Fe, STO:Mn) to -260 K (STO:Ni), while quantum temperature T_1 changes from 150 K (STO:Co) to 225 K (STO:Fe). No apparent correlation with the values reported for STO:M films on sapphire substrates can be seen. However, if in crystals $T_1 < 2T_C$ is the condition for ferroelectric phase formation, then the difference $2T_C - T_1$ can be used to gauge the combined influence of the destabilizing factors. Therefore, our STO films are farther from the phase transition, than crystalline STO. The use of MgO instead of sapphire as a substrate for polycrystalline STO films increases the dielectric contribution of the soft mode, which is beneficial for applications in electronic and microwave devices.

The spectra of the real and imaginary parts of dielectric permittivity of pristine STO and weakly doped polycrystalline STO:M (M = Fe, Ni, Mn, Co) thin films on MgO substrates have been determined by time-domain terahertz spectroscopy. A single absorption band was observed and identified as a ferroelectric soft mode in all films, and the soft mode parameters were obtained for temperatures between 4 and 300 K. The frequency and the dielectric contribution of the soft mode retain the Barrett-like behavior typical for quantum paraelectrics, like crystalline SrTiO₃ or KTaO₃. Large difference between the Curie temperature T_C and the Barrett temperature T_1 indicate that the thin films are farther from the ferroelectric phase transition than crystals. Doping further suppresses the soft mode in

STO, reducing low-temperature dielectric contribution from 350 ± 10 in pristine film to $\approx 250 \pm 10$ in doped films. Our results show the absence of a significant effect of the choice of doping metal on the magnitude of the dielectric contribution, which distinguishes the STO films on MgO from the previously studied STO films on sapphire.

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Conflict of interest. The authors of this work declare that they have no conflicts of interest.

1. J. H. Barrett, Phys. Rev. **86**, 118 (1952).
2. J. Petzelt, T. Ostapchuk, I. Gregora et al. (Collaboration), Phys. Rev. B **64**, 184111 (2001).
3. T. Ostapchuk, J. Petzelt, V. Železny et al. (Collaboration), Phys. Rev. B **66**, 235406 (2002).
4. J. Petzelt, T. Ostapchuk, I. Gregora, M. Savinov, D. Chvostova, J. Liu, and Z. Shen, J. Eur. Ceram. Soc. **26**, 2855 (2006).
5. M. V. Talanov, A. I. Stash, S. A. Ivanov, E. S. Zhukova, B. P. Gorshunov, B. M. Nekrasov, V. Stolyarov, V. Kozlov, M. Savinov, and A. Bush, J. Phys. Chem. Lett. **13**, 11720 (2022).
6. A. Tkach, P. M. Vilarinho, and A. Kholkin, Ferroelectrics **304**, 87 (2004).
7. M. Savinov, V. A. Trepakov, P. P. Syrnikov, V. Železny, J. Pokorny, A. Dejneka, L. Jastrabik, and P. Galinetto, J. Phys. Condens. Matter **20**, 095221 (2008).
8. A. Tkach, P. M. Vilarinho, A. L. Kholkin, A. Pashkin, S. Veljko, and J. Petzelt, Phys. Rev. B **73**, 104113 (2006).
9. S. Maletic, D. Maletic, I. Petronijevic, J. Dojcilovic, and D. M. Popovic, Chin. Phys. B **23**, 026102 (2013).
10. S. Kojima, *2022 Photonics & Electromagnetics Research Symposium (PIERS)*, IEEE, Hangzhou, China (2022).
11. J. Petzelt and S. Kamba, Ferroelectrics **503**, 19 (2016).
12. I. Katayama, H. Shimosato, M. Ashida, I. Kawayama, M. Tonouchi, and T. Itoh, J. Lumin. **128**, 998 (2008).
13. E. S. Zhukova, B. M. Nekrasov, M. Tyunina et al. (Collaboration), J. Alloys Compd. **976**, 173255 (2024).