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FIR and near-millimetre dielectric response of $SrTiO_3$, $BaTiO_3$ and BST films and ceramics

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Abstract

The dielectric response of $Ba_{1-x}Sr_xTiO_3$ ceramics and films ($x = 0$, 0.9, 1) was studied with a particular attention to the soft mode behaviour in the far IR and near-mm range and its comparison with the single crystal behaviour. To analyse the response quantitatively, we used commercial Fourier transform IR and monochromatic backward-wave-oscillator spectroscopy in both transmission and reflection modes and a rigorous evaluation. The soft-mode behaviour is extremely sensitive to the sample quality, particularly in films, and correlates with the lower low-frequency response. The most important factors for this behaviour in the polycrystalline films are grain boundaries and porosity and nano-cracks, which often appear in thicker polycrystalline films along some of the grain boundaries. The brick-wall model for grain boundaries and cracks discussed within the generalized effective medium approximation appears to be appropriate for describing the observed phenomena. In quasi-epitaxial films the macroscopic tensile stress, which influences the phase diagram very sensitively and induces ferroelectricity even in the pure $SrTiO_3$, seems to play the most important role. From the soft-mode behaviour and its splitting, it appears that in the studied $BaTiO_3$ films all the phase transitions, as in single crystals, seem to be present, but smeared with phase coexistence regions down to 10 K. In the quasi-epitaxial BST-0.9 film a smeared ferroelectric transition appears near 150 K.

Keywords: $BaTiO_3$; $SrTiO_3$; Dielectric properties; IR spectroscopy; Grain boundaries; Porosity

1. Introduction

Microwave (MW) dielectric properties of materials are basically determined by higher-frequency, i.e. submillimetre and far-infrared (FIR) absorption processes and in well-processed ceramics can be even extrapolated from the known dielectric response in this range.[1–3] In high-permittivity materials like ferroelectrics the main absorption mechanism is the low-lying polar lattice-vibration mode, mostly strongly temperature dependent, called soft mode. Therefore studying its properties is of crucial importance for understanding MW behaviour of these materials.

$Ba_{1-x}Sr_xTiO_3$ (BST-x) is a very popular high-permittivity system for MW applications, particularly in the thin film form.[4] Therefore we decided to study the soft-mode behaviour in this system. Since it is well known that the low-frequency dielectric properties of thin films substantially differ from those of the bulk (lower permittivity, higher losses),[5] our goal is to compare the soft-mode behaviour in films and bulk materials (crystals, ceramics).

It is well known that in the crystal form the dielectric response of $SrTiO_3$ (STO) is basically determined by the underdamped ferroelectric soft mode parameters in the whole frequency range below about 5×10^{12} Hz,[6–8] and no dielectric dispersion below the soft-mode frequency occurs, at least above the antiferrodistortive transition near 105 K. Also the MW losses in STO single crystals in this temperature range seem to be of intrinsic two-phonon origin.[9] Recently, we have shown[10,11] that essentially the same conclusion is valid also for undoped and dense STO ceramics, even if the low-temperature permittivity values are substantially reduced compared with single crystals. The reduction was shown to be caused by grain-boundary regions with a reduced local permittivity (stiffened local soft-mode response) due to their non-zero polarization. They are probably also one of the reasons for the higher MW losses in ceramics.[7] Grain-boundary effects play an even more important role in polycrystalline STO thin films, as very recently established by Ostapchuk et al.[12] and will be briefly discussed also in this paper.

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In $BaTiO_3$ (BTO) the situation is more complex since the paraelectric–ferroelectric transition near 400 K is of mixed displacive and order-disorder nature, the soft mode is overdamped[13] and the question about additional dielectric dispersion of the central-mode type is still under debate.[14–19] It appears that at least in the $\varepsilon_c(\omega)$ spectrum along the spontaneous polarization P_S in the tetragonal ferroelectric phase an additional dispersion should be responsible for the temperature dependence of the clamped permittivity $\varepsilon_c(T)$[18–21] in agreement with the thermodynamic theory based on the eight-site order-disorder model,[22] since the phonon contribution is temperature independent and amounts to ~30 only. Experiments[18,19] allow estimation of the corresponding relaxation frequency into the 10 GHz range, but reliable data are very scarce and do not exist above 10 GHz. The reasons for this are the difficulty to obtain strictly single-domain samples and the huge dielectric anisotropy $\varepsilon_a/\varepsilon_c \approx 30$, which, together, cause leakage of the much stronger ε_a response into that of ε_c,[20] and the existence of a surface layer from the polishing procedure.[19] Concerning the strong ε_a response, it appears that the overdamped soft phonon (the corresponding relaxation frequency hardens from ~14 to 18 cm^{-1} approaching T_C from room temperature) accounts for the whole clamped permittivity [$\varepsilon_a(RT) \approx 2100$, $\varepsilon_a(380\ K) \approx 1000$),[17–19,23] at least away from T_C, and the published relaxations[14,15] are probably spurious. The same seems to be true in the paraelectric phase[16] (see also Ref 24). Due to the large dielectric anisotropy below T_C, no reliable spectroscopic data on soft modes are so far available for BTO ceramics. In the tetragonal and rhombohedral phase it should be treated as a two-component composite and the effective dielectric spectrum should be treated by various effective medium approximations.[25]

The mixed BST-x system was systematically studied only for ceramics concerning the dielectric and ultrasonic properties to determine the phase diagram.[26] It appears that for composition BST-0.8 all three ferroelectric transitions from the BTO side and the structural transition from STO side merge into a single point near 110 K. No reliable data on the soft mode behaviour are available. In the thin-film form many dielectric data appeared during recent years, but mostly in the standard frequency range below ~1 MHz. In all cases the permittivity is substantially reduced and the anomalies at phase transitions smeared (or even absent) compared with ceramics.

As a first step of our investigations we decided to study the pure STO, BTO and mixed BST-0.9 composition.

2. Experimental

The samples were dense bulk ceramics and various thin films. Most of the films are polycrystalline chemical-solution deposited (CSD) and one set of films is quasi-epitaxial (composed of two types of epitaxial single crystalline grains of ~100 nm size, rotated with each other by 60°), injection metal-organic chemical vapour deposited (MOCVD). All the films were deposited directly on (0001)-oriented sapphire substrates. This enabled us to study their FIR response using convenient transmission techniques[27–29] since the sapphire is transparent in the FIR range and optically isotropic in this orientation.[27] The experiments were performed on Fourier transform interferometer Bruker IFS 113v and in the low-frequency part using a more accurate monochromatic backward wave oscillator spectrometer Epsilon. Transmittance spectra of the films were fitted with a common damped harmonic-oscillator model to determine the transverse optic (TO) mode parameters and the complex dielectric response function. The rigorous formula for the transmittance of a coherent beam through a two-slab system was used. More detailed results on STO films were published elsewhere.[12]

3. Results and discussion

Fig. 1 shows the resulting FIR dielectric spectra of the MOCVD epitaxial 290 nm thick STO film (STO1) at selected temperatures. It is clearly seen that at about 125 K a splitting into three components appears. The main, middle, component looses its strengths on cooling whereas both subsidiary components increase and all components harden. We assume that at ~125 K a ferroelectric transition appears simultaneously with the

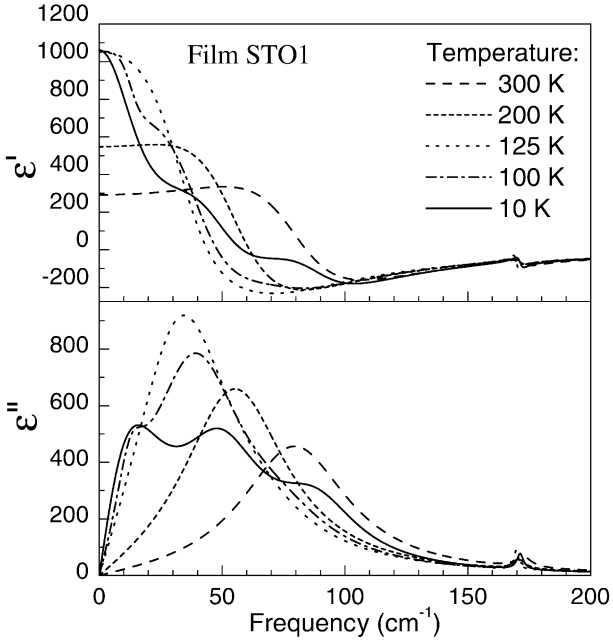

Fig. 1. Real and imaginary part of the dielectric function of STO1 film at selected temperatures.

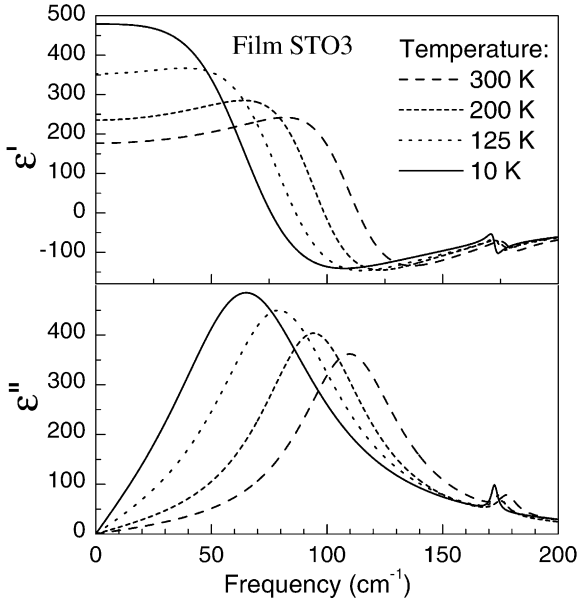

Fig. 2. Real and imaginary part of the dielectric function of STO3 film at selected temperatures.

antiferrodistortive one. The tendency to ferroelectric transition is also seen from the fact that in the whole paraelectric phase the soft mode frequency is lower than that for the STO single crystal. The new components below 125 K are the structural soft-mode doublet, which becomes coupled with the ferroelectric soft mode and activates itself in the IR response. The existence of such a transition can be theoretically expected due to the presence of macroscopic in-plane tensile stress of about 0.7 GPa[30] (detected by XRD) caused by the thermal dilatation coefficient of sapphire (which is smaller than in STO) on cooling from the deposition temperature of 800 C. The assumed polarization vector lies in the film plane.

In contrast to the epitaxial film, the polycrystalline CSD films do not show a macroscopic ferroelectric transition. In Fig. 2 we present the FIR dielectric spectra of a thicker film STO3 (thickness 680 nm). In contrast to STO1, the soft-mode frequencies are appreciably higher and more damped than in single crystal and cease to soften below ~100 K. There is also a remarkable difference between the thinner STO2 (360 nm) and thicker STO3 film in that the soft mode in the latter film is more stiffened at all temperatures. Appearance of forbidden IR modes in micro-Raman spectra of both films indicates local polar regions at room temperature which become stronger on cooling. This effect is qualitatively similar to STO ceramics,[11] but stronger, and can result from polar grain boundaries.[11] The stronger effect can be understood from the smaller grain size in our films (50–100 nm) compared to ceramics (1000–2000 nm) and therefore larger relative volume of grain-boundary regions.

The most striking feature is the higher soft mode frequency in CSD films, which is responsible for the lower low-frequency permittivity. After a careful analysis of all possible reasons we came to conclusion that the dominant effect originates from pores and crack-type nano-porosity at some of the columnar grain boundaries. Porosity, which has somewhere the tendency to percolate along grain boundaries was observed in both polycrystalline films and in the thicker film cracks, forming a ~10 μm net along grain boundaries (Fig. 3). We approximated both the cases by slabs of air gaps perpendicular to the probing FIR electric field described by the brick-wall model (essentially an equivalent circuit of series bulk STO and air capacities) to estimate the influence on the effective soft-mode response and analysed this model from the point of view of generalised effective-medium approximation.[31] For small porosity, this model yields the same results as a more theoretically justified (isotropic) and analytically calculable model of coated-spheres geometry.[32] The effect of small amounts of porosity on the static permittivity and soft mode

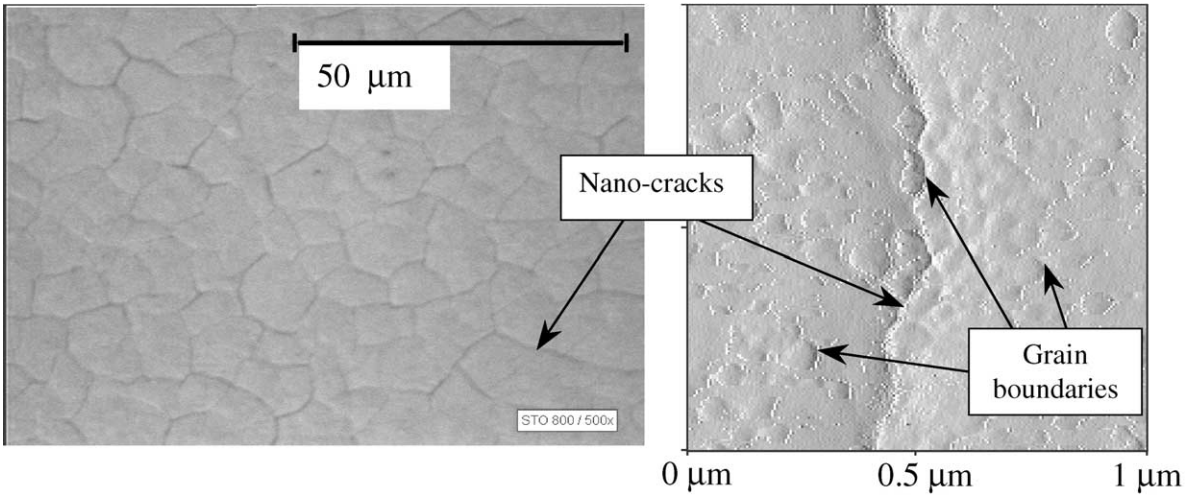

Fig. 3. Optical microscope and AFM picture of the crack-type porosity in the STO3 film.

frequency using the STO single crystal data at 300 and 10 K and both models (with identical results) are shown in Fig. 4. It is seen that our soft-mode frequency results can be explained by assuming an air-gap porosity of 0.2 and 0.4% for the STO2 and STO3 film, respectively, so that, taking into account the density of cracks, their estimated thickness is several nm. Such small porosity may easily escape attention, but nevertheless drastically reduces the permittivity and increases the soft-mode frequency. Physically, this strong effect is mainly because the grain bulk is not macroscopically percolated, some grains are almost separated by cracks where the influence of the depolarization field is very strong. It should be stressed that our FIR experiment probes the in-plane dielectric response (unlike standard dielectric measurements), which may play an important role in the case of columnar boundaries and cracks so that the effective dielectric response could be strongly anisotropic (the out-of-plane response being not so much reduced).

Next let us discuss data for BTO films. The dielectric spectra of the epitaxial MOCVD 200 nm thick film (BTO1) are shown in Fig. 5. It should be mentioned that above 300 K the sapphire substrate of our films becomes almost opaque above 200 cm^{-1}. Saturation of the dielectric constant above 450 K indicates a smeared para-ferroelectric phase transition in the vicinity of this temperature. It corresponds to the single-crystal paraelectric-tetragonal transformation[21,23] at 408 K. Unlike the behaviour in single crystals, the lowest TO1 frequency is somewhat stiffened and temperature independent in the whole temperature region, which results in its lower low-frequency permittivity, but due to this mode overdamping the results are not as accurate as for the STO films. The lowest-frequency TO1 mode stiffening is apparently a result of the depolarization fields due to the existence of domains and anisotropic grains in the ferroelectric phases.[25] Its strength gradually decreases on cooling from the para–ferroelectric transition, but the data down to the lowest temperature indicate a broad coexistence of the rhombohedral and some of the other phases because in the rhombohedral phase both the single-crystal soft-mode components are stiffened to 250 cm^{-1} at least.[23] As the detected residual stress[33] was very weak in comparison with that for the STO1 film, its

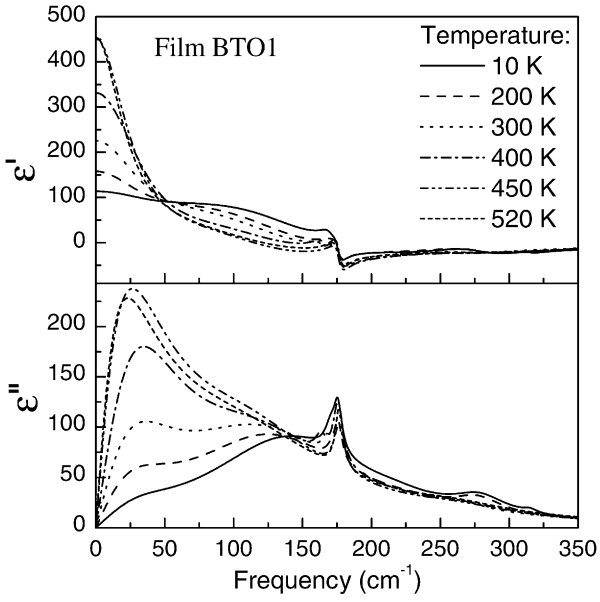

Fig. 5. Real and imaginary part of the dielectric function of BTO1 film at selected temperatures.

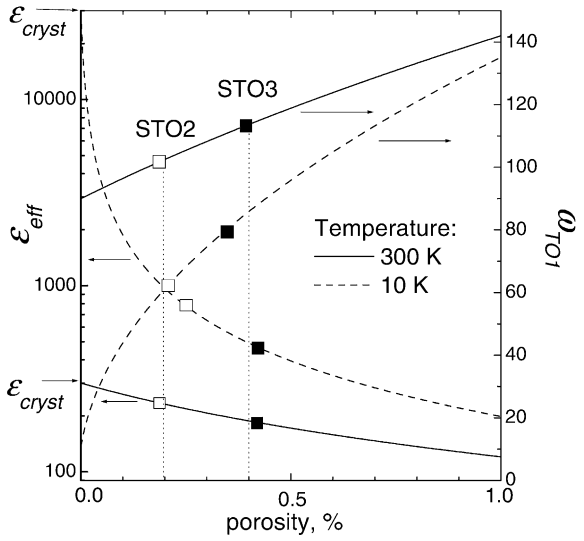

Fig. 4. Effective permittivity and corresponding soft-mode eigenfrequency as a function of porosity, as calculated from the brick-wall model.

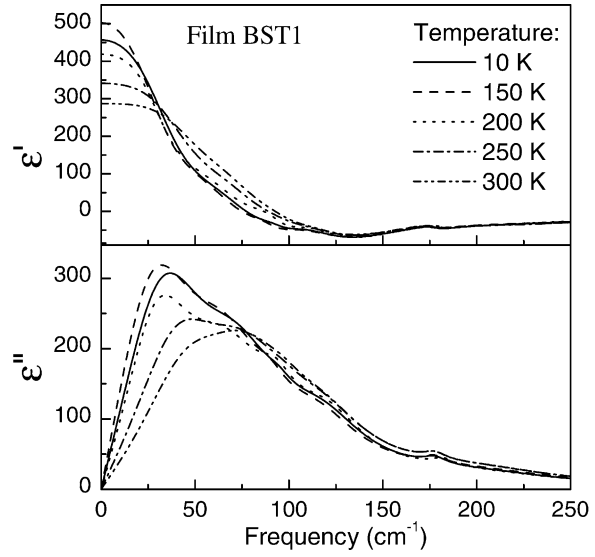

Fig. 6. Real and imaginary part of the dielectric function of BST1 film at selected temperatures.

influence on the film properties is not considered. The CSD films (375, 750 nm) demonstrate qualitatively similar behaviour.

In Fig. 6 we present our dielectric spectra of epitaxial MOCVD BST-0.9 420 nm thick film (BST1). The low-frequency permittivity displays a maximum near 150 K indicating the ferroelectric transition. The lowest-frequency soft mode is broader than in STO, similar to that of BTO, and achieves a minimum frequency of 40 cm^{-1} near 150 K; below this temperature it stays constant. Another mode of similar behaviour and comparable strength lies between 80 and 70 cm^{-1}, similar to that of pure STO. In bulk ceramics of the same composition the smeared ferroelectric transition appears near 80 K.[26] We assign the shift of the ferroelectric transition to higher temperature to the tensile residual stress.[33] Based on our Raman data, it appears also that the antiferrodistortive deformation coexists with the ferroelectricity. The CSD films show broader response without indication of any clear phase transition.

4. Conclusions

Our FIR results for STO show that in epitaxial films the tensile macroscopic strain resulting from the different thermal dilatation of film and substrate promotes the existence of ferroelectricity. In polycrystalline CSD films the grain boundaries and the nano-cracks along some of them, which relax the macroscopic strains, strongly increase the effective soft-mode frequency and reduce the dielectric permittivity and their temperature dependences. This can be understood from the strong effect of the depolarization fields at the cracked boundaries and can be quantitatively accounted for by the simple brick-wall model. In the epitaxial BTO films (almost unstrained) the ferroelectric phase transitions are revealed, but with a broad coexistence of different phases. Behaviour of the polycrystalline BTO film is qualitatively similar. In the epitaxial BST film again the ferroelectricity is promoted due to the presence of tensile strain, and the paraelectric soft-mode is split into STO-like and BTO-like components. Dielectric spectra of the polycrystalline CSD films are more smeared and do not show any clear macroscopic phase transition.

Acknowledgements

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