

Submillimeter and Far Infrared Dielectric Response of Bi-Doped SrTiO₃ Ceramics

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Dielectric response of (Sr_{1-1.5x}Bi_x)TiO₃ ($x = 0.0067\text{--}0.167$) ceramics was investigated by means of Fourier transform infrared (FTIR) spectroscopy and time-domain terahertz spectroscopy (TDS) in the temperature range 20–295 K. Compared to the pure strontium titanate ceramics, the spectra of the doped samples demonstrate: (i) suppression of the soft mode softening, (ii) progressive increase of a relaxation-like dispersion in the millimeter-wavelength region with increasing Bi-doping, and (iii) shift to the lower frequencies of the IR-activated E_g -symmetry structural soft mode. Physical mechanisms responsible for these phenomena are considered.

Keywords: Submillimeter spectroscopy; relaxor ferroelectrics; ceramics

INTRODUCTION

Dielectric properties of (Sr_{1-1.5x}Bi_x)TiO₃ (SBiT-x) were first investigated by Scanavi et al. [1] and recently have attracted interest as typical for relaxor ferroelectrics [2]. The main distinguishing features of the relaxor systems are the presence of a diffuse maximum in the temperature dependence of permittivity and a broad spectrum of relaxation frequencies [3, 4].

In undoped SrTiO₃ and KTaO₃ the lowest polar phonon mode frequency decreases (softens) on cooling, but the ferroelectric phase transition is suppressed by the quantum fluctuations [5] and sample remains paraelectric down to 0 K. The static permittivity is completely defined by the contribution of the polar phonon modes (mostly the soft mode). Doping with off-center impurities like Li in KTaO₃ and Ca or Bi in SrTiO₃ leads to the strong relaxational contribution to the static permittivity [2, 6, 7]. At the same

time, the soft mode contribution becomes smaller. Corresponding hardening of the soft mode frequency with increasing Li content in KTaO_3 has been measured by hyper-Raman [8] and inelastic neutron scattering [9]. Preliminary data on the soft mode behaviour in Bi-doped SrTiO_3 system have been recently reported by some of us [4]. In this paper we present more detailed analysis of the submillimeter and far-infrared measurements on SBiT ceramics with Bi concentration up to 16.7%, which allows us to determine all the frequencies of IR-active excitations.

EXPERIMENTAL PROCEDURE

Six SBiT- x ceramic samples ($x = 0; 0.0067; 0.0267; 0.08; 0.133; 0.167$) were measured down to 20 K by means of Bruker IFS 113v Fourier transform spectrometer and custom-made time-domain terahertz transmission spectrometer [10]. Far IR reflectivity was measured in the range 20–650 cm^{-1} . The complex permittivity was directly measured by transmission TDTS in the frequency range 3–30 cm^{-1} . Thin plane-parallel platelets of 8 mm diameter and 75 and 130 μm thickness were used for this purpose. The obtained reflectivity spectra were normalised to corresponding submillimeter reflectivity values calculated from the complex permittivity determined by TDTS.

RESULTS AND DISCUSSION

The normalised experimental reflectivity spectra were fitted using submillimeter data with the generalized oscillator model of the dielectric function

$$\begin{aligned}\varepsilon^*(\omega) &= \varepsilon'(\omega) - i\varepsilon''(\omega) \\ &= \varepsilon_\infty \prod_{j=1}^n \frac{\omega_{LOj}^2 - \omega^2 + i\omega\gamma_{LOj}}{\omega_{TOj}^2 - \omega^2 + i\omega\gamma_{TOj}} + \frac{f_0}{\omega_0^2 - \omega^2 + i\omega\gamma_0},\end{aligned}\quad (1)$$

where $\varepsilon_\infty = 5.3$ is the permittivity at frequencies above all phonon eigenfrequencies, ω_{TOj} and ω_{LOj} are the eigenfrequencies of the transverse and longitudinal j -th phonon mode, and γ_{TOj} and γ_{LOj} are the respective damping constants. Additional three-parameter overdamped oscillator mode with frequency ω_0 , damping constant γ_0 ($\gamma_0 > 2\omega_0$) and strength f_0 is added to take into account the relaxational dispersion below phonon frequencies.

Results of the fit are shown in Fig. 1 for SBiT-0 and SBiT-0.0267 ceramics. In the pure SrTiO_3 sample three transverse optic phonon modes TO_1 (soft

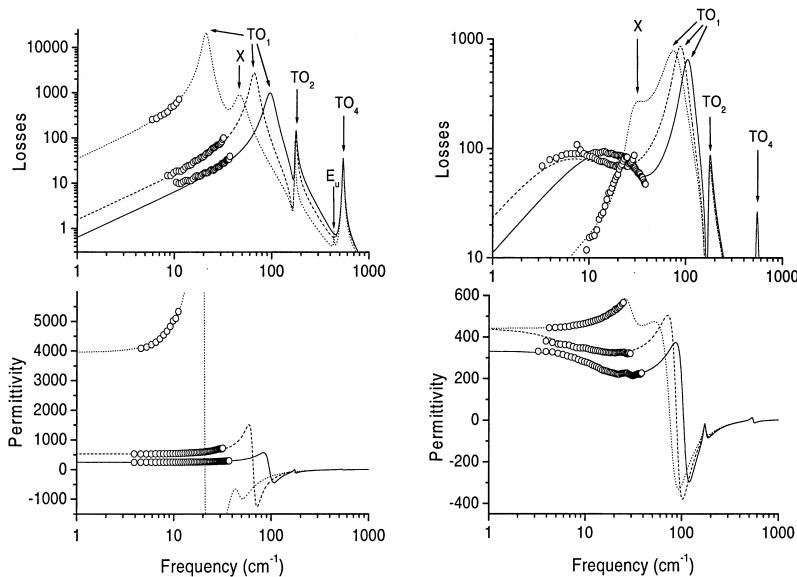


Figure 1. Submillimeter dielectric loss and permittivity (open circles) and IR fits at 295 K (solid line), 160 K (dashed line) and 20 K (dotted line) of pure SrTiO₃ (a) and SBiT-0.0267 (b).

mode), TO₂ (≈ 174 cm⁻¹) and TO₄ (≈ 545 cm⁻¹) are observed in a cubic phase above the structural phase transition ($T_a \approx 130$ K in ceramics) [11]. Below the transition two additional modes appear in the IR spectra due to the Brillouin zone folding: IR-active E_u mode at 435 cm⁻¹ and Raman-active E_g mode (denoted as X-mode) activated in IR due to the coupling with the soft mode which becomes possible in ceramics with frozen polarization at grain boundaries [11]. Bi-doping causes appreciable changes in far IR spectra of SBiT (see Fig. 1b). The soft mode hardens with increasing Bi content and even for $x = 0.0067$ its frequency becomes higher than the X-mode frequency. Simultaneously the X-mode frequency lowers by approximately 10 cm⁻¹ comparing to the pure SrTiO₃ ceramic. It can be understood by the “repulsive” effect that shifts the observed frequencies of two coupled modes with respect to their bare (uncoupled) values. For the undoped ceramics, the soft mode lies below the E_g mode and the resulting X-mode frequency is shifted to higher values. On the contrary, for SBiT samples the soft mode lies above the E_g mode and the X-mode frequency is expected to be lower than the bare frequency.

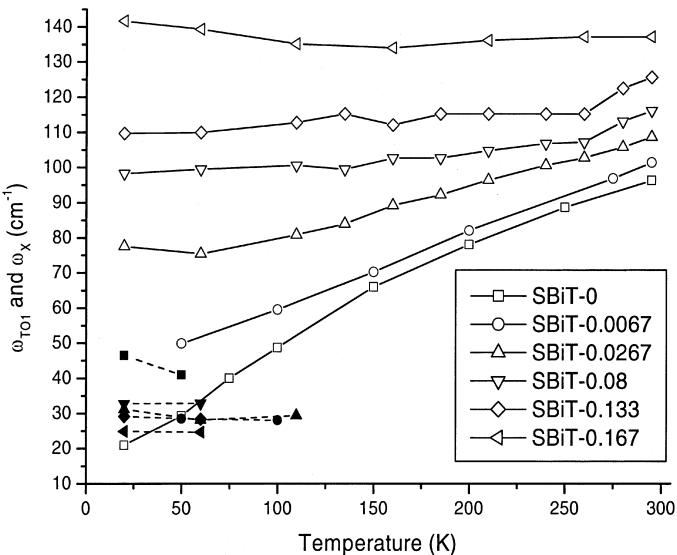


Figure 2. Temperature dependence of the soft mode TO_1 (open symbols) and the X-mode (full symbols) frequencies in SBiT.

Temperature dependences of the X-mode and soft mode frequencies for all investigated SBiT samples are shown in Fig. 2. One can see that for $x \geq 0.08$ the soft mode below room temperature becomes almost temperature independent. Nevertheless its frequency hardens with increase of bismuth content and reaches the level of 140 cm^{-1} for SBiT-0.167. The X-mode frequency in SBiT does not depend on bismuth content within the experimental and fitting errors. On the other hand, the dielectric strength of X-mode distinctly decreases with increasing bismuth content. Unfortunately, the precision of our fits was not high enough for quantitative estimation of the coupling constant. From the qualitative point of view one can expect an increase of the coupling constant for higher doping by the off-center impurities such as bismuth that tends to distort local lattice symmetry. At the same time, the soft mode hardening induced by the doping diminishes the coupling effect and correspondingly the transfer of the effective charge from the soft TO_1 to the X-mode. The latter factor seems to be dominant in SBiT with $x > 0.0267$.

Let us now discuss the relaxational dispersion in SBiT ceramics. It is well known that the dielectric relaxation in SBiT spans over wide frequency range (especially at low temperatures) [3, 4]. However it was not confirmed

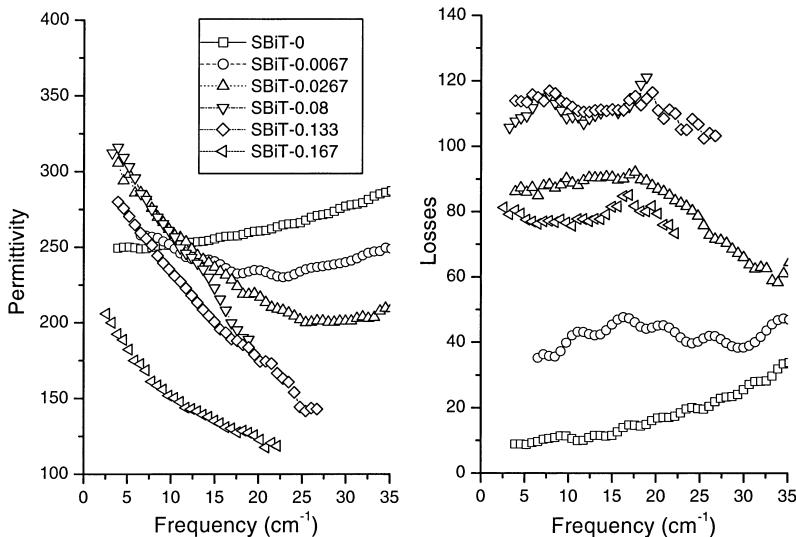


Figure 3. Submillimeter dielectric permittivity and losses of SBiT ceramics at room temperature.

up to now if relaxation-like dispersion reaches millimeter and submillimeter range. Our measurements reveal this type of dispersion in all investigated SBiT samples. Room temperature submillimeter permittivity and losses of all samples are shown in Fig. 3. In contrast to pure SrTiO₃, SBiT samples demonstrate appreciably higher losses and negative slope in the permittivity dispersion. The origin of this dispersion can be attributed to the relaxational hopping of individual (uncorrelated) bismuth ions between the off-center equilibrium positions as the fastest possible polarization process below the optic phonon frequencies. Dielectric losses of SBiT increase with doping for $x \leq 0.08$ and start to decrease above this level. This gives the evidence that at high concentration of Bi ($x > 0.08$) the interaction energy between Bi ions becomes higher than the energy of room temperature thermal fluctuations and the most part of ions are involved in slow polarization processes which do not contribute to submillimeter losses. However quantitative analysis of these effects needs to include dielectric data in the wide frequency range (from 100 Hz to 1 GHz) and will be published in another communication [12].

The relaxation-like character of the submillimeter dispersion is confirmed by its temperature evolution. Namely, by the temperature dependence of relaxation parameters: dielectric contribution $\Delta\epsilon_r$ and relaxation frequency ω_r related to the parameters of the overdamped oscillator in Eq. 1 by the

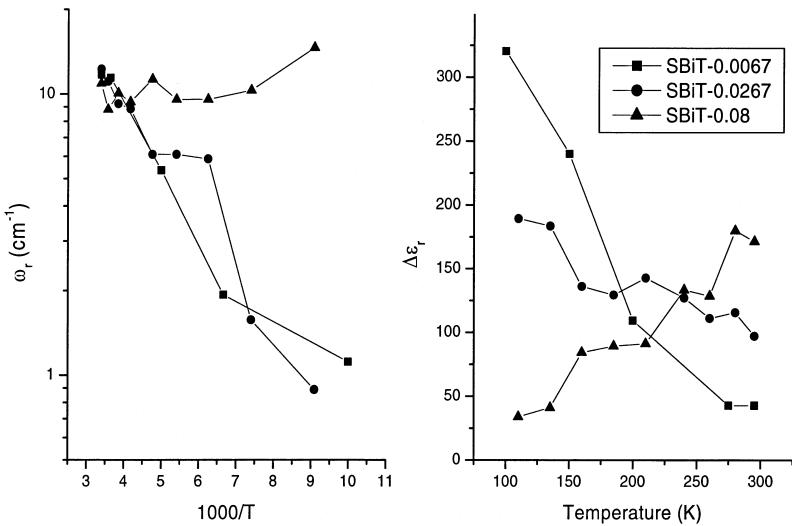


Figure 4. Temperature dependence of the relaxation frequency (a) and dielectric contribution (b) of the overdamped oscillator from Eq. 1 for the fits of SBiT-0.0067, SBiT-0.0267 and SBiT-0.08.

following expressions:

$$\begin{aligned} \Delta\epsilon_r &= f_0/\omega_0^2, \\ \omega_r &= \omega_0^2/\gamma_0. \end{aligned} \quad (2)$$

Results of the fits for three selected concentrations of bismuth are shown in Fig. 4 down to 100 K. The relaxation frequencies of SBiT-0.0067 and SBiT-0.0267 roughly obey the Arrhenius law and the corresponding dielectric contributions increase on cooling. It is in agreement with a simple picture of thermally activated relaxation where the Arrhenius law for relaxation frequency and the Curie law for the dielectric contribution are valid. However, the activation energies that we found from our data (≈ 450 K for SBiT-0.0267) do not correspond precisely to the values found from the microwave data (700–750 K) [4]. Nevertheless it does not make a contradiction because in the investigated frequency range the energy of thermal fluctuations is comparable to the activation energy that can lead to a deviation from the Arrhenius law. In SBiT-0.08 the relaxation frequency is almost temperature independent and dielectric contribution decreases on cooling. Such an unusual behavior is the consequence of strong random fields and correlation

between dipoles in SBT that essentially broaden the distribution of relaxation times. In this case, the model of single relaxation is not valid anymore and the observed behaviour is defined only by the high-frequency tail of the broad distribution of relaxation frequencies.

CONCLUSIONS

The bismuth doping of SrTiO₃ ceramics leads to the hardening of soft mode frequency and suppression of its temperature dependence. The frequencies of other IR active mode are almost independent on Bi content. The coupling of the soft mode with E_g -symmetry Raman doublet in SBT- x decreases due to the soft mode hardening for $x \geq 0.0267$. Dielectric relaxation related to the thermally activated hopping of the off-center bismuth ions appears in all SBT samples below the soft-mode frequency. The anomalous behaviour of the submillimeter losses and fitting parameters of relaxation indicates the presence of cooperative phenomena in SBT systems.

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