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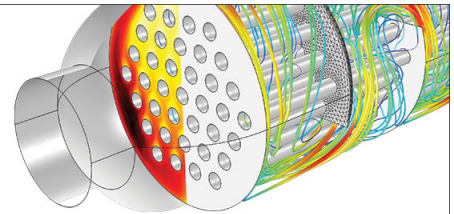
Ferroelastic phase in SrBi$_2$Ta$_2$O$_9$ and study of the ferroelectric phase-transition dynamics

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Polarized microscope observation of ferroelastic domains in a SrBi$_2$Ta$_2$O$_9$ (SBT) single crystal reveals the presence of domains up to $T_{c1} \simeq 770$ K, which supports the ferroelasticity and Amam symmetry of the intermediate phase between ferroelectric and paraelectric phases. Far-infrared spectra of SBT ceramics, single crystal and thin films show a well underdamped optical soft mode at 28 cm^{-1}, which partially softens to 21 cm^{-1} near the ferroelectric transition temperature ($T_{c2} \cong 600$ K). This softening does not explain the entire anomaly of low-frequency permittivity observed near T_{c2}. On the basis of high-frequency measurements, which do not show a significant dispersion, central-mode-type dispersion in the 10–100 GHz range is proposed as an explanation. So, the phase transition at T_{c2} apparently shows a crossover behavior between the displacive and the order–disorder type. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1498005]

SrBi$_2$Ta$_2$O$_9$ (SBT) is currently widely used for nonvolatile ferroelectric (FE) memories due to its polarization fatigue-free nature and low coercive field for polarization switching.[1,2] Although ferroelectricity in SBT was discovered at the beginning of the 1960's,[3,4] and hundreds of papers have been published in the last few years, basic structural and physical properties of SBT are still not completely understood. SBT belongs to the Aurivillius family of bilayered pseudoperovskite oxides. The perovskite-type groups [SrTa$_2$O$_7$]$^{2-}$ and [Bi$_2$O$_2$]$^{2+}$ are stacked alternately along the pseudotetragonal c axis.[5,6] The Bi$_2$O$_2$ layers and TaO$_6$ octahedra are considerably distorted and atomic displacements along the a axis give rise to spontaneous polarization.[7] The FE phase crystallizes in the orthorhombic space group A2$_1$am with two formula units in primitive unit cell ($Z_{prim} = 2$) and transforms to the paraelectric phase (PE) with tetragonal structure I4/mmm ($Z_{prim} = 1$) near 600 K.[5–7] Samples often grow nonstoichiometrically (particularly the Sr and Bi sites) which strongly influences the FE transition temperature T_{c2},[7,8] e.g., $T_{c2} \simeq 750$ K for Sr$_{0.5}$Bi$_{2.3}$Ta$_2$O$_9$.[9] Recently, an intermediate phase between the FE and PE phases has been suggested on the basis of structural and specific heat measurements, however, its space group was not determined.[10,11] Very recently, Hervoches *et al.*[12] published powder neutron diffraction data of Sr$_{0.85}$Bi$_{2.1}$Ta$_2$O$_9$ and suggested the Amam space group for this phase is between 550 and ~820 K. On the other hand, Kim *et al.*[9] proposed a

polar symmetry B2cb for this phase, but their structure remains polar up to 1273 K, which seems very unlikely.

The dynamics of the FE phase transition in SBT has been investigated by Raman scattering.[13–15] An optical soft mode (SM) was observed in the FE phase spectra below 30 cm^{-1}, however, it softens only partially and disappears from the Raman spectra already 50 K below T_{c2}. The SM in the FE phase is expected to be active in both IR and Raman spectra.[16] Moret *et al.*[16] reported IR reflectivity and transmission studies on FE SBT, but their work did not extend into the far-IR SM region. In the mid-IR, they found that the high-frequency (HF) modes in SBT showed the strong influence of the pseudotetragonal parent symmetry (e.g., approximate Raman IR mutual exclusion), but this will not extend to the symmetry-breaking SM.

In this letter, we report on direct observation of ferroelastic domains in a SBT crystal in its intermediate phase, and on the study of the phonon SM in the far-IR spectra. Also, temperature dependence of the complex dielectric response up to 1.8 GHz in the temperature range of 300–570 K will be briefly discussed.

Two types of SBT samples were investigated: Single crystal, as used in a previous study,[16] and ceramics. The single crystal, a plate with dimensions of about 2 mm ×2 mm×0.1 mm, was grown from the melt:[5] Its large face was perpendicular to the c axis. SBT ceramics were prepared by a standard calcination technique and sintered at 1100 °C for 1 h.

IR spectra (15–3000 cm^{-1}) were obtained using a Fourier transform spectrometer Bruker IFS 113v. IR reflectivity
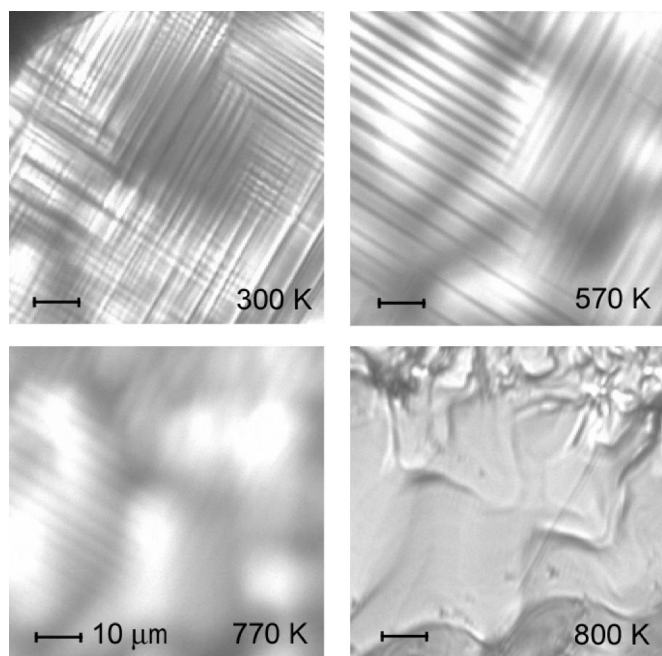
FIG. 1. Images of SBT single crystal at selected temperatures in polarized microscope. Ferroelastic domain structure disappears between 770 and 800 K.

was studied between 30 and 568 K using a cryostat and custom-made furnace, transmission spectra of the thin films were investigated up to 673 K using a commercial high-temperature cell (Specac P/N 5850). Above room temperature, a polyethylene filter was used to reduce the radiation from the sample, nonetheless, the thermal radiation entering the interferometer from the heated sample was taken into account in our evaluation. Dielectric measurements in the HF range of 1 MHz–1.8 GHz were performed using a computer controlled dielectric spectrometer with the HP 4291B Impedance Analyzer, the Novocontrol BDS 2100 coaxial sample cell and the Sigma System M18 temperature chamber for temperatures 300–570 K.

Ferroelastic domains were investigated in the single-crystal sample at temperatures up to 870 K using a Leica DMLP polarized microscope equipped with Linkam THMS 600 temperature cell (see Fig. 1). It can be seem that the domains do not vanish at the FE phase transition ($T_{c2} \simeq 600$ K) but remain at least up to ~770 K. At 800 K, no domain pattern was observed. The gradual disappearance of domains on heating indicates that the transition from ferroelastic to paraelastic phase (770 K$<T_{c1}<$800 K) is near second order. Both possible space groups (Amam and B2cb) of the intermediate phase[9,12] can be ferroelastic and both phases have a doubled-primitive unit cell compared with the high-temperature tetragonal phase I4/mmm. On one hand, no spontaneous polarization has been reported above T_{c2}. On the other hand, a small signal of second-harmonic generation was observed between T_{c2} and T_{c1} (Ref. 17) which could be evidence for the presence of small polar regions or clusters in the intermediate phase. The A2$_1$am space group of the FE structure is not a subgroup of the B2cb space group, therefore, it is difficult to understand the Curie–Weiss anomaly near T_{c2} and we suggest the Amam symmetry for the intermediate phase. This implies that the upper transition at T_{c1} is
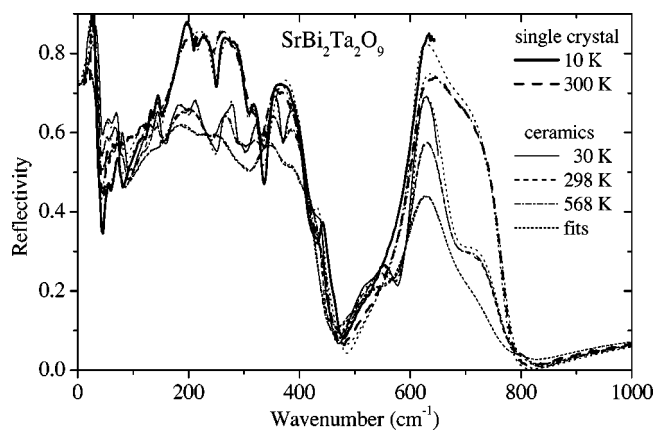

FIG. 2. Temperature dependence of the IR reflectivity spectra of SBT ceramics and single crystal. Single-crystal spectra are taken at polarization of IR beam perpendicular to *c* axis.

improper ferroelastic[18] (doubling of the unit-cell volume) and the lower one at T_{c2} is proper FE (no further change of the primitive unit-cell volume). No change of domain structure is seen at and below T_{c2}, which supports our conclusion.

The temperature dependence of the IR reflectivity spectra of SBT ceramics and single crystal is shown in Fig. 2. The spectra were taken below 650 cm^{-1}, which is the transparency region of the polyethylene windows in the cryostat and the polyethylene filter used for reduction of the IR emission from the hot sample. Only the room-temperature spectrum was obtained up to 3000 cm^{-1} and because no pronounced changes are expected in the mid-IR range, the room-temperature reflectivity above 650 cm^{-1} was used for the fits of the spectra at all temperatures. The room-temperature spectrum above 200 cm^{-1} agrees with that in Ref. 16. The reflection bands are best resolved in the low-temperature spectra where the mode dampings are smaller. We resolved 24 modes in reflectivity of ceramics at 30 K, however, the factor group analysis in the A2$_1$am space group predicts 61 IR active modes (21 A$_1$ + 19 B$_1$ + 21 B$_2$). The reflectivity of the SBT single crystal revealed 14 modes at 10 K, although 42 modes are allowed (B$_1$ modes can not be seen on this (001) oriented single-crystal plate). Not all modes are resolved in the spectrum because of possible mode overlapping and/or their small intensities. The increase of damping with temperature causes the broadening of the bands and decrease of their intensity. The highest achieved temperature, 568 K, is close to T_{c2}. The reflectivity was fitted with the sum of classical damped oscillators (dotted lines in Fig. 2) and we used 24 and 20 modes for the fit of the lowest- and highest-temperature reflectivity, respectively.

The real (ε') and imaginary (ε'') part of the complex permittivity computed from the reflectivity fit of ceramics are shown in Fig. 3. One can see that the lowest-frequency phonon gives the highest contribution (~100) to the static permittivity ε_0 and it is well underdamped at most temperatures, although its damping increases upon heating. The frequency of the mode softens from 28 cm^{-1} at 30 K to 21 cm^{-1} at 568 K. The SM frequency ω_s obeys the Cochran law $\omega_s^2 = A(T_c-T)$ with $T_c = 1420$ K and $A = 0.5536$ K^{-1}. Similar temperature dependence of the SM was observed also in Raman scattering,[13] but the SM frequency and its
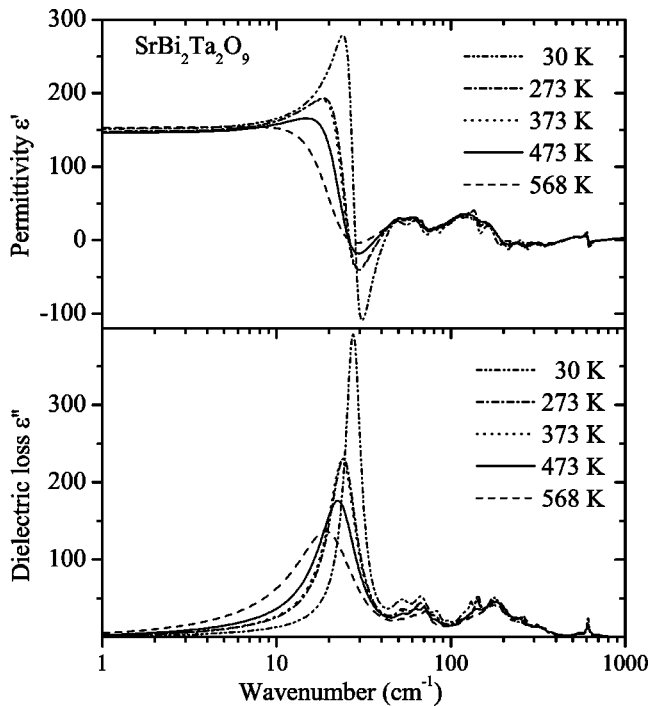
FIG. 3. Temperature dependence of the complex permittivity of SBT ceramics obtained from the fits of IR reflectivities.

damping were slightly higher (see Fig. 4). Unlike in IR, the SM is not active in the Raman spectra above T_{c2}, therefore its intensity decreases upon heating. This causes smearing of the Raman band at high temperatures which could be fitted by an apparent increase of the damping and less accurate evaluation of the eigenfrequency. The discrepancy between the ω_s by both experimental techniques could also be ex-

plained by the different samples used. Our value and temperature dependence of ω_s was confirmed by submillimeter transmission measurements on SBT thin films (the details will be published later). Concerning the SM assignment, Stachiotti *et al.*[19] theoretically studied lattice dynamics of SBT and found one unstable phonon mode whose eigenvector mainly involves movements of the Bi atoms relative to the TaO_6 perovskite-type blocks.

Partial softening of ω_s on heating to T_{c2} causes only small increase of ε_0 which can not explain the dielectric anomaly near T_{c2} $[\varepsilon_0(T_{c2}) \cong 500-800]$.[3,4] Central-mode-type anomaly (i. e., dielectric relaxation below phonon frequencies) should be responsible for the low-frequency dielectric anomaly. To estimate its frequency, we performed dielectric measurements in the 100 Hz–1.8 GHz frequency range from room temperature up to 570 K. Only a small dispersion was seen at high temperatures below 50 MHz which was, however, not connected with the critical slowing down. This means that the central mode must lie substantially above 2 GHz but certainly below 300 GHz. Because of the presence of a phonon SM as well as a central-mode-type dispersion, the FE phase transition shows a crossover between displacive and order–disorder behavior.

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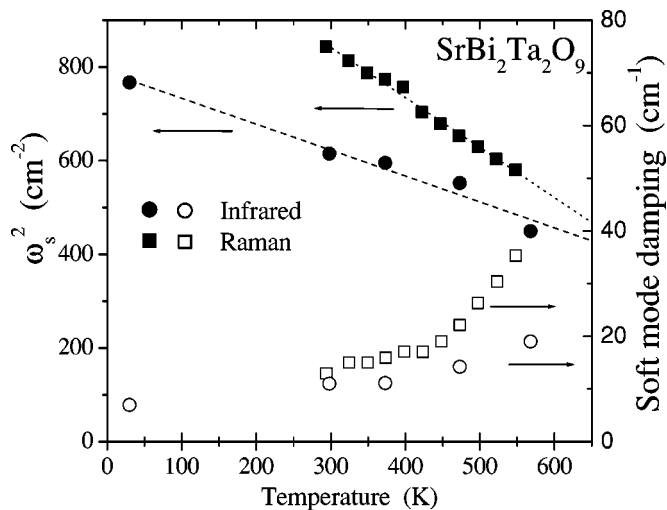

FIG. 4. Temperature dependence of the SM frequency squared observed in IR and Raman spectra together with the SM dampings. (Raman data are from Ref. 13.)