Low-temperature nanospectroscopy of the structural ferroelectric phases in single-crystalline barium titanate

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1 Fourier-transform infrared spectroscopy

We performed a Fourier-transform infrared spectroscopy (FTIR) study of the (111)-oriented BTO crystal at temperatures of 300 K, 230 K, and 150 K. Figure S1 (a) shows the reflectivity spectra obtained in the spectral regime from 1.5 to 25 µm. The spectral region from 17 to 23 µm is of special interest as here, the highest-frequency phonon mode is located. This region is marked by dashed lines in figure S1 (a) and a zoom of the reflectivity spectra in this regime is presented in figure S1 (b). We observe a significant dip of the reflectivity at 300 K (red curve) at a wavelength of 21.2 µm. This dip shifts to 21 µm at 230 K (orange curve) and splits into two minima at 150 K (green curve), located at 20.8 µm and 21.6 µm. The positions of the minima are marked by dashed lines in the color of the respective curve in figure S1 (b).

Fig. S1 LT-FTIR spectroscopy on a BTO-(111) sample. The reflectivity R at 300 K (red), 230 K (orange), and 150 K (green) is shown over the full measureable wavelength range in (a) with the dotted lines marking the region of the phonon resonance. A more detailed spectrum of this region is shown in (b). We observe a splitting of the reflectivity minima at 150 K and a general blue-shift of the short-wavelength minima with decreasing temperature. Please note, that the spectra are recorded on multi-domain crystals and represent a superposition of differently oriented crystal variants.
The spectral position of the phonon mode is consistent with values found in literature\(^1\) including the splitting observed at lower temperatures\(^2\). The latter is attributed to changes in the crystal symmetry upon the phase transitions. The FTIR study has been performed on a multi-domain crystal. Hence, the spectra represent a superposition of differently oriented crystal variants. Determining the spectral dielectric constants by fitting to a Lorentz oscillator model is therefore not possible. Nevertheless, the blue-shift of the phonon mode with decreasing temperature is in agreement with the results of the nanospectroscopy measurements presented in the main article (Fig. 3).

2 Methodology of nanoscopic spectroscopy

In Fig. S2 (a), we present an exemplary linescan measurement in the orthorhombic phase at \(T_{\text{orth}} = 220\text{K}\), showing how the nanospectroscopic information presented in Fig. 3 of the main paper is obtained. A line crossing all domain types is chosen and scanned repeatedly, while the wavelength is reduced in increments of around 0.13 \(\mu\text{m}\) after every ten scanned lines. The near-field signal displayed in Fig. S2 (a) is normalized to the incident power. We observe a resonant behavior and a contrast between different domain types. The line-scan data is analyzed by selecting cross-sections of different domain-types, as shown in Fig. S2 (b). Here, the spectral shift of the near-field response between domain-types and the resulting contrast reversal upon changing wavelengths becomes even more apparent. Multiple such cross-sections are employed to statistically obtain a value of the near-field signal for every wavelength at both domain types.

![Near-field signal (normalized to incident power) on a single line of (111)-oriented BTO at \(T_{\text{orth}}\) with changing wavelength \(\lambda\) (a) and corresponding cross-sections (b). The resonant behavior and the contrast between two different domain-types is clearly observed. The two cross-sections represent the two domain types and reveal a significant spectral shift of the respective near-field responses.](image-url)
3 Additional Scan Data

In the main article, only selected data channels of the 2D-scans are shown in order to keep Fig. 2 compact. In figure S4, we additionally present the original topography as well as the Kelvin probe force microscopy (KPFM) signal.

![Comprehensive 2D scan data. The columns show from left to right the topography, the differential topography, the PFM signal, the second-harmonic demodulated near-field signal, and the KPFM signal. The measurements at $T_{tetra}$, $T_{orth}$, and $T_{rhom}$ are presented in the rows from top to bottom.](image)

We observe similar features in the KPFM channel as in the piezoresponse force microscopy (PFM) and scattering-type scanning near-field infrared microscopy (s-SNIM) scans (see Fig. 2 of the main manuscript for a detailed discussion). However, the KPFM pattern is more complex and domain boundaries appear not as sharp. We attribute the similarities to screening charges depending on the polarization of the domains. Polarization changes caused by ferroelectric phase transitions as well as pyroelectricity upon temperature changes result in a highly charged surface in the orthorhombic and rhombohedral phases compared to the initial tetragonal state as evident by the larger values of the KPFM signal at $T_{orth}$ and $T_{rhom}$. 
From the topography data, we extract the surface roughness in the different phases in terms of the root mean square (Sq) on both, single domain areas and on the full scan area as displayed in Figs. 2 and S3. Both Sq values are listed in Table S1. Please note that due to different inclination angles between certain domains in the different phases, the large-area values include this slope difference of the domains, and consequently depend on the domain size, type and number per sample area.

<table>
<thead>
<tr>
<th>Structural phase</th>
<th>Sq of single domain area [nm]</th>
<th>Sq of full scan area [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal</td>
<td>0.15</td>
<td>0.4</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>0.50</td>
<td>2.0</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>0.60</td>
<td>20.6</td>
</tr>
</tbody>
</table>

**Table S1** Areal surface roughness Sq (root mean square height) extracted from topography images of the different phases as displayed in Fig. S3

While the x-channel of the PFM measurement as presented in Fig. 2 of the main article contains the complete information about the PFM measurement, the display via amplitude and phase is the more common approach in literature. We therefore show the amplitude and phase scan data along with the x-channel scans of the main article for each phase in Fig. S4.

![Fig. S4 PFM amplitude and phase scans for each structural phase corresponding to the PFM x-channel scans presented in Fig. 2 of the main article.](image-url)
References
