Ferroelectric phase transition in polycrystalline $KTaO_3$ thin film revealed by terahertz spectroscopy

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$KTaO_3$ single crystal is an archetypal incipient ferroelectric in which a long-range ferroelectric order does not establish at low temperatures owing to quantum fluctuations. We report on a strong evidence of the ferroelectric phase transition near 60 K revealed by terahertz spectroscopy and microwave permittivity measurements of a polycrystalline $KTaO_3$ thin film on (0001) sapphire substrate prepared by chemical solution deposition. The soft mode behavior is clearly observed in the terahertz (THz) spectra with a minimum frequency at 60 K. At the same temperature microwave permittivity maximum appears. The THz spectra strongly resemble that of strained epitaxial $SrTiO_3/DyScO_3$ films: the ferroelectric soft mode is linearly coupled to a central peak which is silent in the paraelectric phase and it becomes coupled to the polarization below the ferroelectric transition temperature with a progressively increasing bare strength. © *2011 American Institute of Physics*. [doi:10.1063/1.3624710]

Potassium tantalate ($KTaO_3$, KTO) is, similarly to $SrTiO_3$, an incipient ferroelectric compound, in which the quantum fluctuations at low temperatures prevent a displacive ferroelectric phase transition to occur. The static dielectric permittivity obeys the Curie-Weiss law on cooling due to a significant TO_1 ferroelectric soft mode softening,[1,2] and it increases up to ~5000 below 10 K while the structure of single crystalline KTO maintains its perovskite cubic symmetry.[3] External conditions or forces (electric field, doping,[2,4] and strain[5]) may then influence the competition between the ferroelectric ordering and quantum effects and cause the ferroelectric phase transition to appear. In KTO the nonlinear coefficient β, describing the anharmonicity of the soft mode and characterizing the capabilities for voltage-induced tuning of its dielectric properties, reaches a larger value than that of $SrTiO_3$ (Ref. 6), and also the loss tangent ($\tan\delta$) in the microwave range becomes significantly lower below 100 K.[7] These properties make KTO a highly interesting subject of investigation from the point of view of fundamental physics and applications.

In this Letter we follow the temperature dependence of the soft mode in a polycrystalline KTO thin film. The terahertz (THz) spectroscopy technique covers the pertinent spectral range to observe the soft mode and its coupling to a lower-frequency relaxation (central peak): this allows us to observe a ferroelectric phase transition in the film.

The films were prepared by chemical solution deposition. Potassium acetate (99+%, Sigma-Aldrich) and tantalum ethoxide (99.99% H. C. Starck) were dissolved in 2-methoxyethanol (99.3+%, Sigma-Aldrich), refluxed for 24 h, and distilled to remove the by-products. After cooling to room temperature the concentration was adjusted to 0.4 M, and 30% excess of potassium acetate was added to the solution.

The solution was deposited on (0001) sapphire substrates by spin-coating, dried at 180 °C for 2 min on a hotplate, and annealed at 900 °C for 5 min in a rapid thermal annealing furnace with the heating rate of 15 K/s. The procedure was repeated 4 times to increase the film thickness to 200 nm; the final heating at 900 °C was performed for 15 min.

X-ray diffraction (XRD) analysis was performed in a θ-2θ geometry from 5° to 60° with a step and count time of 0.017° and 100 s, respectively, using monochromatic $CuK_{\alpha 1}$ radiation source. The analysis revealed perovskite KTO

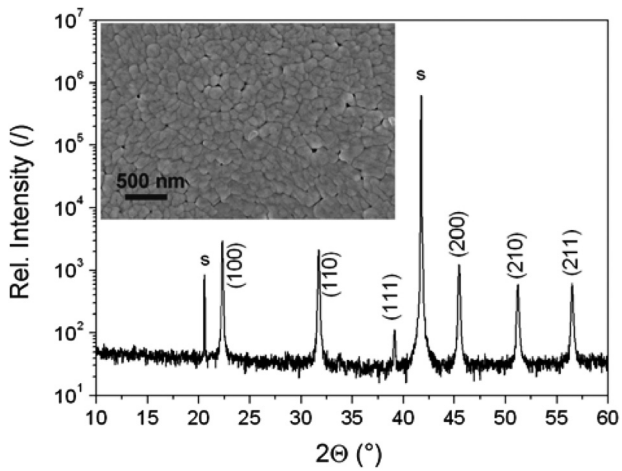

FIG. 1. XRD pattern of the KTO thin film deposited on (0001) sapphire. Peaks of the substrate are denoted as *S*. All other peaks correspond to the perovskite $KTaO_3$ phase.[8] Plain-view FE-SEM micrograph of the film is shown in the inset.

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film[8] with preferred (100) orientation (Fig. 1). Field emission scanning microscopy (FE-SEM) was employed to analyze surface morphology of the film. Dense microstructure consists of grains with an average size of 160 nm as obtained by lineal analysis (Fig. 1).

For quantitative chemical analysis by inductively coupled plasma mass spectrometry the solution was dried and heated at 900 °C for 15 min. Besides the main components K and Ta, the analysis revealed the presence of 53 mass ppm of Na and 13 mass ppm of Mg, while other impurities were below 5 mass ppm.

The experiments were performed by using THz time-domain spectroscopy with a custom made setup powered by a femtosecond laser oscillator and described in detail in Ref. 9. The complex transmittance spectra of the thin film sample were obtained in an optical cryostat, and they served for the calculation of the in-plane complex dielectric response in the THz range. These spectra were complemented by dielectric measurements in the gigahertz (GHz) frequency range using a thin dielectric resonator method.[10]

A special care has been paid to the characterization of the substrate thickness in order to obtain accurate quantitative results.[9,11] In Fig. 2(a) we show THz time-domain wave forms obtained at 20 K by transmitting the THz pulse through a bare substrate and through a film deposited on a substrate with the nominally same thickness. We apply the time windowing procedure to the data[12] and evaluate the complex refractive index N of the film or its dielectric permittivity $\varepsilon = N^2$ from the direct pass of the THz pulse (0) and from the first Fabry-Pérot reflection inside the substrate (1). The difference between these spectra is very sensitive to the substrate thickness[9] which can be optimized by minimizing $\sum_i |N^{(0)}(\omega_i) - N^{(1)}(\omega_i)|$; this is demonstrated in Fig. 2(b). In this way we found the difference between the thicknesses of the sapphire wafers to be (2.3 ± 0.2) μm, and this leads to an absolute accuracy of our determination of the permittivity ± 20.

The complex dielectric spectra for several temperatures are shown in Fig. 3. We detect the soft mode in the THz

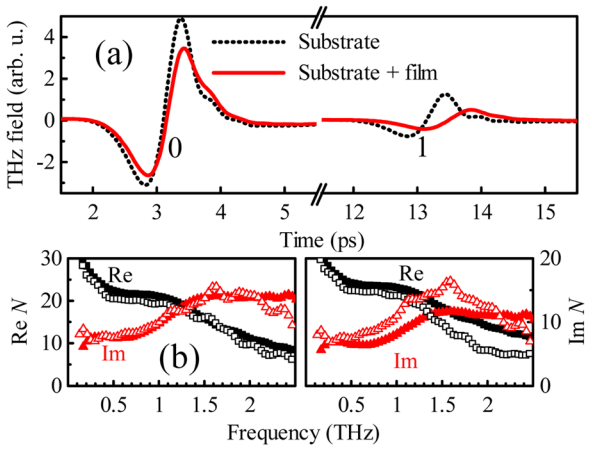

FIG. 2. (Color online) (a) THz time-domain wave forms measured at 20 K with a bare sapphire substrate and with a 200 nm thick KTO film deposited on the substrate; 0: direct pass, 1: first internal Fabry-Pérot reflection. (b) Spectra of complex refractive index obtained from the direct pass (closed symbols) and from the first echo (open symbols). Thicknesses of the two substrates differ by 2.3 μm (left plot) and 0 μm (right plot).

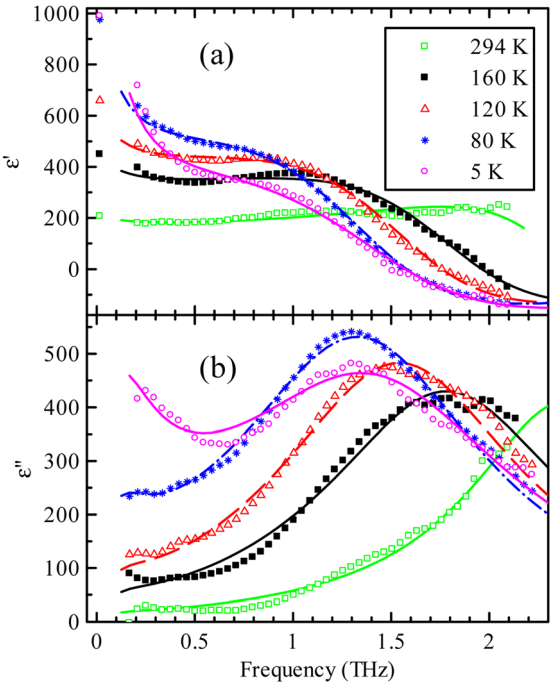

FIG. 3. (Color online) (a) Real and (b) imaginary part of the permittivity of KTO film for selected temperatures; symbols: experiment, lines: fits using Eq. (1). Microwave permittivity at 16 GHz is also shown in (a).

range, and the temperature variation of its frequency is clearly observed. At lower temperatures, as the soft mode softens, an onset of a central peak is seen with a relaxation frequency below the accessible spectral range. Similar behavior has been observed in various films and multilayers of $SrTiO_3$ deposited on $DyScO_3$ substrates.[11,13] For fitting the spectra we used model of coupled oscillator and Debye relaxation which is able to describe the dielectric function in a large variety of strained $SrTiO_3$ films,[11,13] namely

$$\varepsilon(\omega) = \frac{f(1 - i\omega/\gamma) + g(\omega_0^2 - \omega^2 - i\omega\Gamma) + 2\delta\sqrt{fg}}{(\omega_0^2 - \omega^2 - i\omega\Gamma)(1 - i\omega/\gamma) - \delta^2} + \varepsilon_\infty. \tag{1}$$

A common fit of all the measured spectra has been performed. The parameters of the bare soft mode are its frequency ω_0 and damping Γ (which are both temperature dependent in our fit) and the oscillator strength (temperature independent, $f \approx 1.3 \times 10^6$ cm^{-2} from the fit); the bare central mode is characterized by the temperature independent relaxation frequency γ ($\approx$6 cm^{-1}) and strength g. The coupling constant $\delta \approx 27$ cm^{-1} is found also temperature independent. All these values are very similar to those of $SrTiO_3$ (Ref. 13); also, in analogy with $SrTiO_3$ the effective charge g of the relaxation vanishes in the paraelectric phase but becomes non zero below $\sim$80 K [see Fig. 4(a)] where the central mode starts to dominate in the THz spectra.

In Fig. 4(a) we show the soft mode frequency as a function of temperature which exhibits a minimum near 60 K. Around this temperature the central mode also starts to couple to the polarization. Very similar phenomena have been observed at the ferroelectric phase transition in $SrTiO_3$/$DyScO_3$ system.[13,14] The microwave permittivity measured

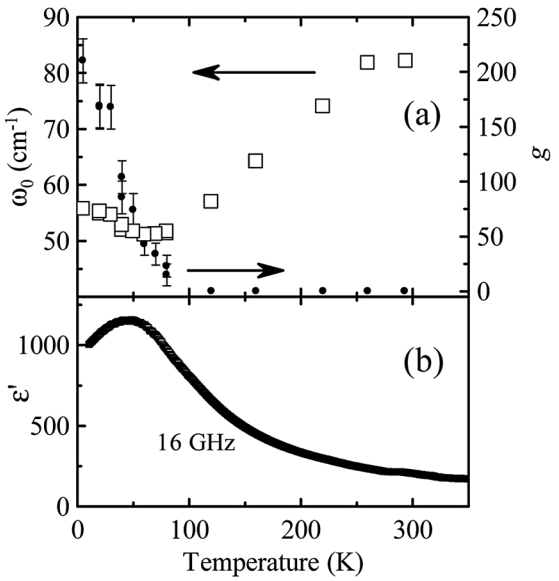

FIG. 4. (a) Soft mode frequency ω_0 and relaxation strength g as a function of temperature obtained from the fits of THz spectra. (b) Real part of the permittivity at 16 GHz.

at 16 GHz is plotted in Fig. 4(b); the curve shows a maximum in the range of 40–60 K. The values above 80 K can be fitted with the Curie-Weiss law $\varepsilon' = C/(T - T_c)$ which yields the Curie-Weiss temperature $T_c \approx 15$ K, indicating a diffuse first-order transition.

The origin of the central mode which appears in the spectra of many ferroelectric materials in the close vicinity of a displacive-type phase transition is still subject of debate.[15–17] Even if central modes can be induced by defects, there are models assuming its intrinsic origin related to a highly anharmonic (multiminimum) form of the soft mode potential.

Incipient ferroelectrics are structurally rather unstable; a mechanical strain or the presence of a small amount of chemical impurities (doping) may induce a long-range ferroelectric order. This was frequently demonstrated in $SrTiO_3$ (Refs. 4 and 5). In our case, quantitative chemical analysis revealed substantially less impurities than the amount which could induce the ferroelectricity.[4] Therefore the main reason for the ferroelectric ordering should be the strain.

In $SrTiO_3$ thin film samples the in-plane ferroelectric order can be induced for a quite small value of the tensile strain.[5] Very recently Tyunina *et al.* reported about an appearance of the ferroelectric phase transition in an epitaxial film of KTO on a $SrTiO_3$ substrate.[18] In this case a large in-plane compressive strain (−2.1%) led to a T_c as high as 700 K. The thermal expansion coefficient of sapphire is larger than that of KTO; thus, cooling the sample after its processing at 900 °C may induce a compressive in-plane strain in the film. By analogy with $SrTiO_3$, such a strain would induce a transition into the ferroelectric phase with a spontaneous polarization predominantly perpendicular to the film plane. The THz spectra are then sensitive mostly to the *E*-component of the soft mode.

Ferroelectric soft mode in polycrystalline KTO film deposited on Si and SiO_2 was previously investigated by Železný *et al.* using the far infrared (IR) transmission spectroscopy.[19] They did not reveal any phase transition but found a remarkable stiffening of the soft mode; its frequency then decreases only down to ~55 cm^{-1} at 10 K, which is close to the value that we have observed. Note that the soft mode softens down to 20 cm^{-1} in KTO single crystal.[20] Similar soft mode stiffening was observed also in $SrTiO_3$ films, and it was explained in the frame of effective medium approximation by the presence of low-permittivity grain boundaries and possible nano-crack-type porosity which strongly reduce the effective dielectric response.[21]

To summarize, we characterized the dielectric properties of a polycrystalline KTO film on (0001) sapphire in the THz range. Our results emphasize the key role of the soft mode, which shows a classical softening down to 60 K and below it hardens. This is in agreement with the permittivity measurements at 16 GHz. An existence of the central peak coupled to the soft mode has been revealed. The data provide a strong indication that a ferroelectric phase transition occurs near 60 K.

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