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Terahertz Spectroscopy of Ordered $PbSc_{1/2}Nb_{1/2}O_3$ Ceramics

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The ordered $PbSc_{1/2}Nb_{1/2}O_3$ ceramics were studied by THz transmission spectroscopy in the temperature range of 80–300 K. Below ferroelectric phase transition temperature the strength of central mode gradually decreases and gives evidence for a mixed displacive and order–disorder character of the transitions. Ferroelectric phase transition is connected with an abrupt freezing and rise of polar nanoregions into ferroelectric domains.

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1. Introduction

Relaxor ferroelectrics or relaxors are a class of disordered crystals possessing peculiar structure and properties. At high temperature they exist in a nonpolar paraelectric phase, similar to the paraelectric phase of normal ferroelectrics in many respects. Upon cooling they transform into an ergodic relaxor state in which polar regions of nanometer scale appear with randomly distributed directions of dipole moments. This transformation at the so-called Burns temperature (T_B) [1] cannot be considered as a structural phase transition because it is not accompanied by any change of crystal structure on the macroscopic or mesoscopic scale. Nevertheless, the softening of some modes, inherent feature of displacive ferroelectric phase transition, is also observed in the ferroelectric relaxors [2].

Dielectric properties of $PbSc_{1/2}Nb_{1/2}O_3$ (PSN) are highly dependent of B site (Sc^{3+} and Nb^{5+}) ions order. If these ions are statistically disordered, PSN exhibits relaxor ferroelectric behavior above the ferroelectric phase transition (380 K) [3]. However, if the ions are 1:1 chemically ordered (this can be achieved by a

proper annealing), PSN shows only a sharp ferroelectric transition, and its temperature shifts down to 340 K [3]. Experimental results of dielectric spectroscopy (up to 1 GHz) of ordered PSN ceramics are discussed in terms of distributions of relaxation times [4]. One must note, however, that its temperature dependence is less expressed, since ferroelectric dispersion mainly appears in region of several GHz and several tens of GHz.

The aim of this paper therefore is to investigate dynamics of ferroelectric phase transition in ordered PSN ceramics by THz transmission spectroscopy.

2. Experimental

Figure 1 represents a conventional experimental setup for time-resolved coherent THz spectroscopy. A Ti:sapphire laser delivers pulse of 120 fs duration at a wavelength of 800 nm with 80 MHz repetition rate. The beam is splitted into two parts: the first one excites a low-temperature grown (LT) GaAs-based emitter, while the second, time-delayed pulse, gates the LT GaAs-based detector. Therefore, correlation of excitation and detection pulses allows one to monitor the

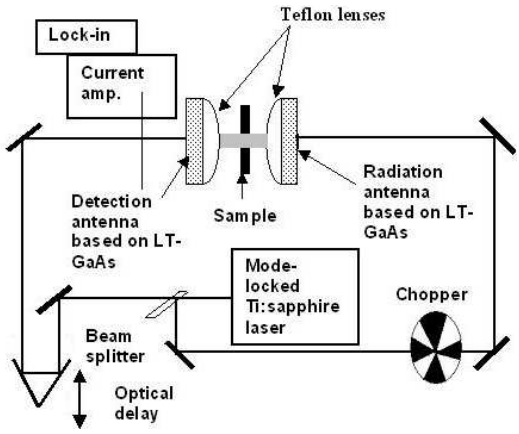

Fig. 1. Experimental setup for time-resolved THz spectroscopy.

evolution of the THz signal directly in the time domain. The emitted THz radiation of about 1 mm diameter was collimated by teflon lenses. After fast Fourier transform, the signal was normalized with respect to the reference — the signal without sample. Free standing samples with apertures of 2 mm and 40 μm thick were placed in the beam path, and the transmitted signal was recorded. A cryostat with thin teflon windows was used for measurements down to 80 K.

3. Results and discussion

The THz spectra of ordered PSN ceramics are presented in Fig. 2. Two contributions can be observed at lower frequencies in these spectra — the main

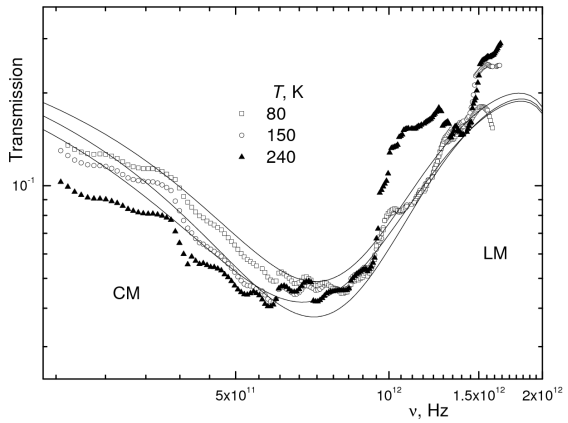

Fig. 2. THz transmission spectra of ordered PSN ceramics at various temperatures. Solid lines are results of the fits.

ferroelectric dispersion (central mode) and phonon contribution at higher frequencies. Phonon contribution in this frequency range is mainly caused by a vibration of rigid BO_6 octahedra against Pb atoms (the Last mode (LM) [5]). These two contributions can be easily separated by using an oscillator law of dielectric function

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{\omega_{01}^2 - \omega^2 + \mathrm{i}\omega\gamma_1} + \frac{\Delta\varepsilon_2}{\omega_{02}^2 - \omega^2 + \mathrm{i}\omega\gamma_2}, \tag{1}$$

where ω_{0i} is the resonance frequency, γ_i is the damping of the i-th oscillator and $\Delta\varepsilon_i$ is (reduced) i-th oscillator strength. In the case of a homogeneous sample, the complex refraction index $N = n - \mathrm{i}k$ is related to the complex transmission through

$$T(\omega) = \frac{4N\exp(\mathrm{i}\omega(N-1)d/c)}{(N+1)^2} \sum_{k=0}^{m} \left[\left(\frac{N-1}{N+1}\right)\exp(\mathrm{i}\omega N d/c)\right]^{2k}, \tag{2}$$

where d is the sample thickness, c is the light velocity and m labels number of reflections in the sample. These reflections are experimentally resolved (at least for thick samples) and form separate pulses in the measured signal, so that the value of the coefficient m can be easily determined. The fit of (1) and (2) describes THz spectra of PSN ceramics quite good (Fig. 2, solid lines). The obtained parameters of this fit are following: $\varepsilon_\infty = 100$, $\omega_{01} = 30$ cm^{-1}, $\gamma_1 = 36$ cm^{-1}, $\Delta\varepsilon_2 = 150$, $\omega_{02} = 80$ cm^{-1}, $\gamma_2 = 10$ cm^{-1}, only $\Delta\varepsilon_1$ changes with temperature (Fig. 3) according to the Curie–Weiss law

$$\Delta\varepsilon = \frac{C}{T_\mathrm{c} - T}, \tag{3}$$

where C is the Curie–Weiss constant and T_c denotes the Curie–Weiss temperature. The obtained parameters are $C = 83800$ and $T_\mathrm{c} = 390$ K. These values indicate a mixed character of ferroelectric phase transitions. Similarly to other disorder

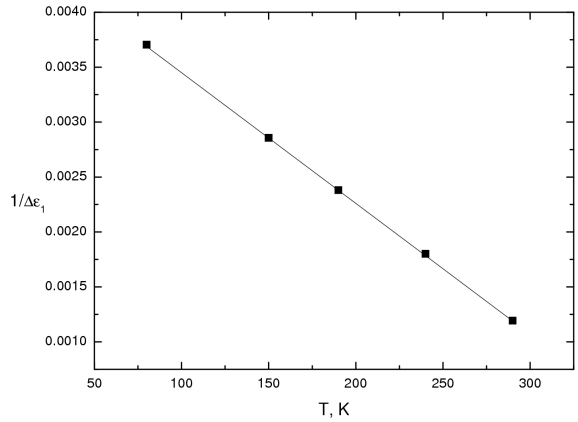

Fig. 3. Currie–Weiss fit of $\Delta\varepsilon_1$.

ferroelectrics [6] one can conclude that the ferroelectric transition in PSN ordered ceramics is connected with an abrupt freezing and rise of the clusters into domains and the classical division of phase transitions into displacive and order-disorder ones is no more sufficient.

Acknowledgments

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