Polar Phonons in Relaxor Ferroelectric 0.2PSN–0.4PMN–0.4PZN

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Relaxor ferroelectrics $0.2PbSc_{1/2}Nb_{1/2}O_3-0.4PbMg_{1/3}Nb_{2/3}O_3-0.4PbZn_{1/3}Nb_{2/3}O_3$ ceramics were studied by means of the Fourier transform infrared reflection and THz transmission spectroscopy in the temperature range of 20–500 K. On heating from low temperatures, the A_1 component of the strongly split TO_1 mode softens towards the Burns temperature, but the softening ceases near 400 K, which could be a signature of polar cluster percolation temperature.

PACS numbers: 78.30.–j, 63.20.–e, 71.55.Jv

1. Introduction

Solution of relaxor enigma is still one of the most challenging problems in the physics of ferroelectrics. Since the discovery of the archetypical relaxor material $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) [1], the origin of its key features — (i) anomalous broad dielectric dispersion at low temperatures, (ii) non-ergodic behavior, and (iii) virtually no symmetry breaking after zero field cooling down to the lowest temperatures — has been interpreted controversially. No breaking of cubic symmetry was observed at any temperature in PMN in absence of bias electric field [2]. However, for $PbSc_{1/2}Nb_{1/2}O_3$ (PSN) and $PbZn_{1/3}Nb_{2/3}O_3$ (PZN) a ferroelectric phase transition from cubic to rhombohedral phase was reported near 378 K [3] and 410 K [4], respectively. Ternary solid solutions of PSN–PZN–PMN relaxor ferroelectrics have been first synthesized and investigated by Dambekalne et al. [5]. Results of broadband dielectric spectroscopy of some PMN–PSN–PZN ceramics have been already published [6].

The aim of the present work is to investigate infrared (IR) and THz spectra of 0.2PSN–0.4PMN–0.4PZN relaxor ceramics with emphasis on discussion of activities and temperature dependences of optic phonons in IR spectra.

2. Experimental

The ternary 0.2PSN–0.4PMN–0.4PZN solid solution was synthesized by solid state reactions from high grade oxides PbO_3, Nb_2O_5, MgO, ZnO, Sc_2O_3 [5]. Measurements at THz frequencies from 3 cm^{-1} to 30 cm^{-1} (90–900 GHz) were performed in the transmission mode using a time-domain THz spectrometer based on an amplified femtosecond laser system. IR reflectivity spectra were obtained using a Fourier transform IR (FTIR) spectrometer Bruker IFS 113v in the frequency range of 20–3300 cm^{-1} (0.6–100 THz) above room temperature, at lower temperature the reduced spectral range up to 650 cm^{-1} was investigated because this is the transparency region of polyethylene windows in the cryostat (Oxford Inst.).

3. Results and discussion

IR and THz reflectivity spectra of 0.2PSN–0.4PMN–0.4PZN ceramics taken at various temperatures are shown in Fig. 1. Reflectivity spectra below 30 cm^{-1} were calculated from THz transmission spectra. The spectral range above 800 cm^{-1} is not shown because the reflectivity is almost flat at higher frequencies, approaching the value given by the high-frequency permittivity ε_∞. IR reflectivity
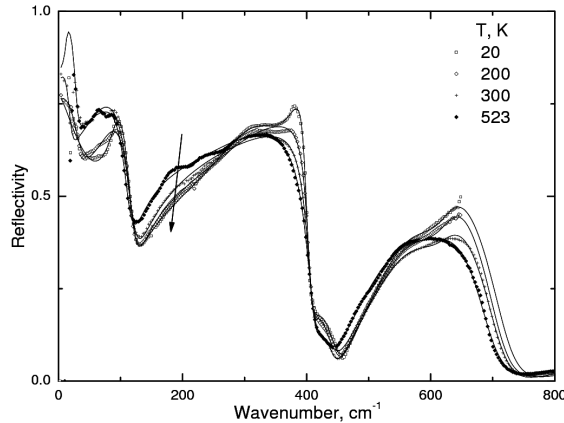

Fig. 1.   IR and THz reflectivity spectra of 0.2PSN–0.4PMN–0.4PZN ceramics at various temperatures. Solid lines are results of the fits.

and THz dielectric spectra were fitted simultaneously, using a generalized-oscillator model of the factorized form of the complex permittivity:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{\mathrm{LO}j}^2 - \omega^2 + \mathrm{i}\omega\gamma_{\mathrm{LO}j}}{\omega_{\mathrm{TO}j}^2 - \omega^2 + \mathrm{i}\omega\gamma_{\mathrm{TO}j}}, \tag{3.1}$$

where $\omega_{\mathrm{TO}j}$ and $\omega_{\mathrm{LO}j}$ mark the transverse (TO) and longitudinal (LO) frequency of the j-th mode, respectively, and $\gamma_{\mathrm{TO}j}$ and $\gamma_{\mathrm{LO}j}$ denote their corresponding damping constants. $\varepsilon^*(\omega)$ is related to reflectivity $R(\omega)$ by

$$R(\omega) = \left| \frac{\sqrt{\varepsilon^*(\omega)} - 1}{\sqrt{\varepsilon^*(\omega)} + 1} \right|. \tag{3.2}$$

Real and imaginary parts of $\varepsilon^*(\omega)$ obtained from the fits of IR reflectivity and THz dielectric spectra are shown in Fig. 2. Eight polar phonons were resolved in the fits of reflectivity below 150 K and seven modes at higher temperatures. Also
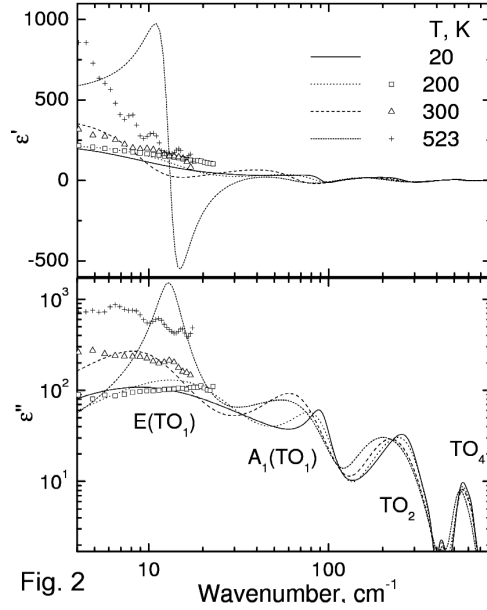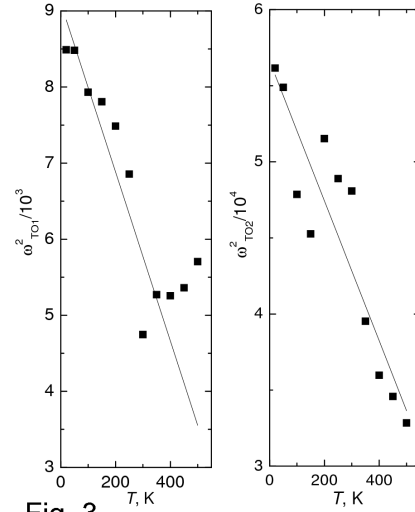

Fig. 2.   Complex dielectric permittivity obtained from the fit of IR and THz spectra of 0.2PSN–0.4PMN–0.4PZN ceramics.

Fig. 3.   Cochran fit to $A_1(TO_1)$ and TO_2 modes in 0.2PSN–0.4PMN–0.4PZN.

interesting phonon anomalies were observed. Most of phonon frequencies exhibit softening up on heating. The most remarkable softening is seen for the lowest frequency $A_1(TO_1)$ phonon (see Fig. 3). Similar soft TO_1 mode (the Last mode expressing predominantly the vibration of rigid BO_6 octahedra against Pb atoms) was observed in PMN and PST [7–10]. This mode was explained as a ferroelectric soft mode in polar clusters [7], which softens close to the Burns temperature. The soft mode frequency follows the Cochran law:

$$\omega_{SM}^2 = A(T_{cr} - T), \tag{3.3}$$

where the constant $A = 11.1$ cm^2/K and $T_{cr} = 820$ K is the critical softening temperature. It is really difficult to assert that this temperature corresponds to the Burns temperature, since the experimental TO_1 frequencies start to increase already above 400 K. We speculate that the T_l temperature corresponds to the temperature, below which the polar clusters are percolated. The effective soft mode cannot completely soften in the system of non-percolated clusters [11] due

to rise of the effective soft phonon frequency in the composite of polar clusters with non-polar matrix. Therefore, the leveling off (or even increase) of the soft mode frequency is seen above $T_l \approx 400$ K.

Surprisingly, the TO_2 polar mode frequency also softens on heating and follows the Cochran law (see Fig. 3). The T_{cr} of TO_2 mode is equal to 1231 K and $A = 45.97$ cm^2/K. This mode is the so-called Slater mode describing predominantly vibration of B atoms against oxygen octahedral [10]. The B sites exhibit large chemical disorder (4 various atoms of different valency!) and the temperature T_{cr} of TO_2 modes can correspond to temperature, at which the B site atoms could migrate, because its value is close to a melting point.

Acknowledgments

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