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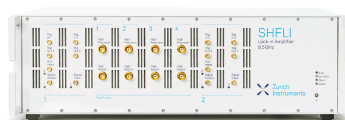
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## Far-infrared soft-mode behavior in $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ thin films

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Temperature dependences of the optic phonons in  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (PST) sol-gel films deposited on sapphire substrates were studied by means of Fourier transform far-infrared transmission spectroscopy in the temperature range of 20–900 K. Four films displaying different *B*-site order with both ferroelectric and relaxor behavior were studied. In all cases the TO mode near  $80\text{ cm}^{-1}$  at 10 K softens on heating to  $\approx 45\text{ cm}^{-1}$  following the Cochran law with extrapolated critical temperature near 700 K which is 400 K above the temperature of dielectric maximum,  $T_m$ . Above 600 K the TO<sub>1</sub> mode remains stable. This mode can be assigned to the  $A_1$  component of the ferroelectric soft-mode inside polar clusters which form below the Burns temperature near 700 K. In the ordered PST film another mode activates below  $T_m$  in the infrared spectra near  $60\text{ cm}^{-1}$ , also exhibiting an anomalous temperature dependence due to its coupling with the former mode. It is assigned to the  $A_1$  component of the  $F_{2g}$  Raman active mode. The central mode, which appears below the Burns temperature in the terahertz range, is assigned to the dynamics of polar clusters. It slows down on cooling and vanishes from our spectral range below  $T_m$ . Another overdamped excitation assigned to the *E* component of the soft mode appears near  $30\text{ cm}^{-1}$  at low temperature. © 2005 American Institute of Physics. [DOI: 10.1063/1.2061895]

### I. INTRODUCTION

Ferroelectric relaxors, in particular, complex perovskites with the general formula  $\text{PbB}_{1/3}\text{B}'_{2/3}\text{O}_3$  and  $\text{PbB}'_{1/2}\text{B}''_{1/2}\text{O}_3$ , are of high interest due to their excellent dielectric, electrostrictive, and pyroelectric properties.<sup>1</sup> A discovery of giant piezoelectric response in relaxor-based crystals by Park and Shrout<sup>2</sup> turned the attention of the scientific community to better understand relaxor ferroelectricity.

Lead magnesium niobate  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) and lead scandium tantalate  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (PST) are model representatives of relaxor ferroelectrics which exhibit high and broad maxima in the real  $\epsilon'(T)$  and imaginary  $\epsilon''(T)$  parts of the dielectric permittivity which shift with the increasing frequency to higher temperatures. No ferroelectric (FE) phase transition occurs in PMN without bias electric field, while PST exhibits a spontaneous FE transition. Its temperature depends on the ordering of *B*-site ions (Sc and Ta). Disordered PST undergoes FE transition at  $T_c \sim 270\text{ K}$ , while  $T_c$  of the ordered sample appears near 300 K without typical relaxor behavior above  $T_c$ .<sup>3,4</sup>

It is well known that the peculiar dielectric properties of relaxors are connected with a broad dielectric relaxation [we call it central mode (CM) in analogy with inelastic scattering experiments] below the polar-phonon frequencies. It stems from the dynamics of nanoscopic inhomogeneities—polar clusters. Low-frequency experimental dielectric data exists on the behavior of the CM in FE relaxors, but much less data were published about the dielectric response in the mega-

hertz and gigahertz range<sup>5,6</sup> and terahertz data are practically missing in the literature. Neutron diffuse scattering in PMN revealed<sup>7</sup> the CM below the Burns temperature,  $T_d=620\text{ K}$ , where the polar nanoclusters appear. However, its frequency was not determined.

Very recently, infrared (IR) transmission and microwave dielectric data<sup>8</sup> of PMN have shown that the CM has a characteristic frequency near  $20\text{ cm}^{-1}$  (0.6 THz) at  $T_d$  and its frequency dramatically slows down to subhertz region on cooling to freezing temperature  $T_f$  near 200 K.<sup>9</sup> Simultaneously the relaxation broadens on cooling, giving rise to the frequency independent losses between 100 Hz and 100 GHz at temperatures below  $T_f$ .<sup>9</sup> Dielectric studies of PST up to 33 GHz revealed a two-component CM,<sup>10,11</sup> however, its behavior at high temperatures near  $T_d$  was not studied. One of the aims of this study is to investigate the CM at high temperatures to confirm its vanishing (merging with the soft-mode response) above  $T_d$ .

The lattice dynamics of PMN were studied by means of Raman, IR, and inelastic neutron scattering spectroscopy.<sup>8,9,12–14</sup> It was shown<sup>8,13</sup> that the lowest-frequency transverse-optic phonon (TO<sub>1</sub>)  $\omega_{\text{SM}}$  follows the Cochran law

$$\omega_{\text{SM}} = A\sqrt{T_d - T}, \quad (1)$$

with the extrapolated critical temperature near the Burns temperature  $T_d=620\text{ K}$ . It indicates that the TO<sub>1</sub> frequency  $\omega_{\text{SM}}$  can be assigned to the FE soft mode (SM) in polar clusters. The questions arise: Is this the general behavior typical for all FE relaxors? What is the behavior of relaxors

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with the spontaneous FE phase transition (PT)? Does the soft mode feel the FE PT temperature  $T_c$  (like in other displacive FEs) or rather the Burns temperature which is typically 300–400 K above  $T_c$ ?

The phonons in bulk PST were already studied by the Raman<sup>15–19</sup> and IR spectroscopy<sup>20,21</sup> and no optic-mode softening was observed. Only small anomalies in phonon frequencies were seen in the Raman and IR spectra near  $T_c$ . From that it was concluded that the transition is of the order-disorder type, which is, however, rather unusual for perovskite FEs.

Also the question of phonon activity in the Raman spectra is of interest. Factor-group analysis for the  $Pm3m$  space group in the paraelectric phase, corresponding to disordered PST, predicts three  $F_{1u}$  only IR active phonons and one silent  $F_{2u}$  mode so that no phonons should be Raman active. Nevertheless, a number of modes were observed in the Raman spectra of paraelectric phase. Siny and Smirnova<sup>16</sup> and independently Bismayer *et al.*<sup>17</sup> explained the activity of the phonons in Raman spectra by doubling of the unit cell in the paraelectric phase due to the 1:1  $B$ -site ordering. In this case the space group is  $Fm\bar{3}m$  and the factor-group analysis yields the following optic vibration modes:

$$\Gamma = A_{1g}(R) + E_g(R) + F_{1g}(-) + 4F_{1u}(\text{IR}) + 2F_{2g}(R) + F_{2u}(-). \quad (2)$$

It means that four Raman and four distinct IR active modes should be expected in the spectra. However, first-order Raman lines are seen not only in  $B$ -site ordered samples, but also in disordered PST and in other relaxors such as PMN. Siny and Smirnova<sup>16</sup> explained this Raman activity by local short-range  $B$ -site ordering in chemical clusters. Namely, Raman scattering is sensitive to short-range (nm) order, as the mode activity is given by the phonon eigenvectors which are determined by the interatomic force constants.

Another assignment was suggested recently by Hlinka *et al.*<sup>22</sup> They argued that Raman scattering in relaxors is primarily due to anisotropic polar clusters rather than to 1:1  $B$ -site ordering. It would mean that the Raman-activated modes belong prevalingly to the Brillouin-zone center of the parent  $Pm3m$  cubic structure rather than to modes activated by the zone folding as it was assumed by Siny and Smirnova.

Also results of the pulsed neutron atomic pair-density function analysis by Egami *et al.*<sup>23</sup> speak in favor of such a picture. They have shown that the Burns temperature  $T_d$  is the local Curie temperature below which the polar clusters are formed, but the local polarization of Pb persists up to  $\sim 1000$  K several hundreds of K above  $T_d$ . Probably both mechanisms of mode activation in the Raman spectra have to be considered and to distinguish between them requires more detailed studies, particularly at very high temperatures near the  $B$ -site ordering temperature. Comparison of the Raman spectra with properly evaluated IR spectra is also necessary.

Factor-group analysis in the  $R3m$  rhombohedral ferroelectric phase with the doubled unit cell due to  $B$ -site ordering yields the following optic modes:

$$\Gamma = 7A_1(R, \text{IR}) + 2A_2(-) + 9E(R, \text{IR}), \quad (3)$$

and  $1A_1+1E$  acoustic modes. It means that up to 16 TO modes simultaneously Raman and IR active plus corresponding 16 LO Raman active modes can be expected in the spectra of the ferroelectric phase. IR active modes in bulk PST ceramics were studied by means of IR reflectivity.<sup>20,21</sup> The spectra revealed correlation between the degree of 1:1  $B$ -site ordering and the appearance of an extra mode at  $315 \text{ cm}^{-1}$ . The high-frequency wing of the CM was observed above room temperature in the reflectivity spectra below  $30 \text{ cm}^{-1}$ . However, the accuracy of IR reflectivity technique is limited at low frequencies and high temperatures. In this case transmission measurements are more accurate and more sensitive to absorption mechanisms, but for this purpose, due to high absorption, thin films are needed. The aim of this study is to investigate temperature dependence of the low-frequency polar phonons and CM in PST films with various  $B$ -site order in a broad temperature interval of 20–900 K. It should allow us to shed more light on the lattice and polar-cluster dynamics between  $T_c$  and the Burns temperature  $T_d$ .

## II. EXPERIMENT

PST thin films were prepared by chemical solution deposition on sapphire substrates, which are transparent in the far IR.<sup>24</sup> Four films of various degree of order were investigated: disordered (annealed at  $700 \text{ }^\circ\text{C}$  for 1 min), slightly ordered (annealed at  $850 \text{ }^\circ\text{C}$  for 1 min), 50% ordered (annealed at  $850 \text{ }^\circ\text{C}$  for 1 h), and 78% highly ordered (annealed at  $800 \text{ }^\circ\text{C}$  for 48 h). The degree of ordering was determined by the x-ray diffraction from  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  superlattice peak intensity and the size of the ordered regions was investigated using transmission electron microscopy (TEM) dark-field imaging.<sup>24</sup> The thickness of the films was about 500 nm, plane-parallel (0001) oriented sapphire substrates were 0.5 mm thick. The unpolarized IR transmission spectra were taken using FTIR spectrometer Bruker IFS 113v at temperatures between 20 and 900 K with a resolution of  $0.5 \text{ cm}^{-1}$ . A helium-cooled Si bolometer operating at 1.5 K was used as detector, an Optistat CF cryostat with polyethylene windows was used for cooling, and a high-temperature cell SPECAC P/N 5850 was used for the heating. The investigated spectral range was limited by the transparency window of the sapphire substrate; at 20 K up to  $450 \text{ cm}^{-1}$  (15 THz), at 900 K the sample was opaque already above  $170 \text{ cm}^{-1}$ .

## III. SPECTRA EVALUATION

IR transmission spectra of 78% ordered PST film at selected temperatures are shown in Fig. 1. Dense oscillations in the spectra are due to interferences in the substrate, while the broad minima correspond to frequencies of polar phonons in the film. Splitting of  $\text{TO}_1$  SM and  $\text{TO}_2$  phonons at 20 K is clearly seen. The spectra were taken at more than 20 temperatures. At each temperature the spectra of a bare sapphire substrate and the PST film on the substrate were measured. The overall transmission decreases on heating, mainly due to the increase in multiphonon absorption of the sapphire substrate. The transmission spectrum of the bare substrate (pub-

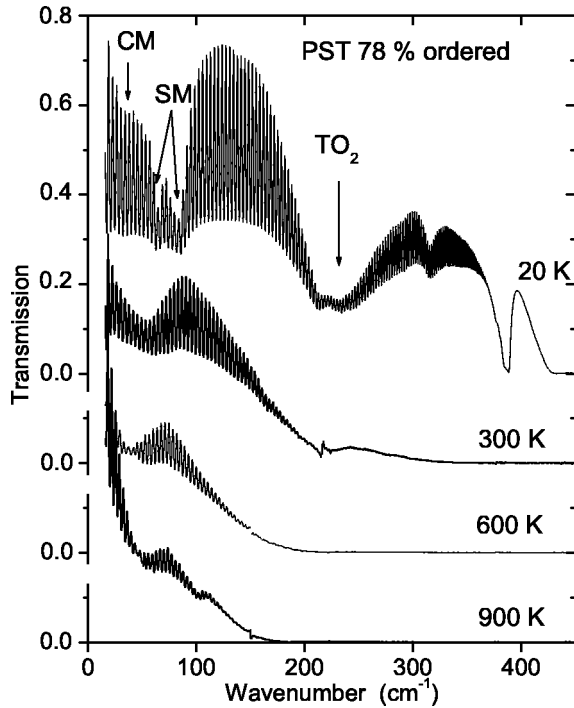


FIG. 1. IR transmission spectra of the 500 nm thick 78% ordered PST film deposited on sapphire substrate (490  $\mu\text{m}$ ) for various temperatures. Frequencies of the central mode (CM), split  $\text{TO}_1$  soft mode (SM), and  $\text{TO}_2$  phonon are marked. Absorption peak near  $380\text{ cm}^{-1}$  is a phonon peak from the sapphire. Small peak near  $220\text{ cm}^{-1}$  at 300 K is an instrumental effect.

lished in Ref. 8) was first fitted with a sum of harmonic oscillators using Fresnel formulas for coherent transmission of a plane-parallel sample (i.e., taking into account the interference effects).<sup>25</sup> The resulting fit parameters of sapphire were then used for the fit of the PST/sapphire two-layer system.

The complex transmittance of the two-layer system was computed by the transfer-matrix formalism method including interference effects.<sup>26</sup> The model of the sum of damped quasi-harmonic oscillators in the form

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \sum_{j=1}^n \frac{\Delta\varepsilon_j \omega_j^2}{\omega_j^2 - \omega^2 + i\omega\gamma_j}, \quad (4)$$

was used for the expression of the complex permittivity  $\varepsilon^*$  of the films.  $\omega_j$ ,  $\gamma_j$ , and  $\Delta\varepsilon_j$  denote the frequency, damping, and contribution to the static permittivity of the  $j$ th polar mode, respectively. The parameter  $\varepsilon_\infty$  describes the high-frequency permittivity originating from the electronic polarization and from the polar-phonons contribution above the spectral range studied.

#### IV. RESULTS AND DISCUSSION

Real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) parts of permittivity  $\varepsilon^*$  of the 78% ordered PST thin film calculated from the fit of transmission spectra in Fig. 1 are shown in Fig. 2. The frequencies of the maxima of  $\varepsilon''$  correspond to the mode frequencies. Parameters of the modes above  $200\text{ cm}^{-1}$  were fixed during our fits at temperatures above 300 K because the substrate was opaque and this range is omitted in the figure. We note that the mode parameters correspond very

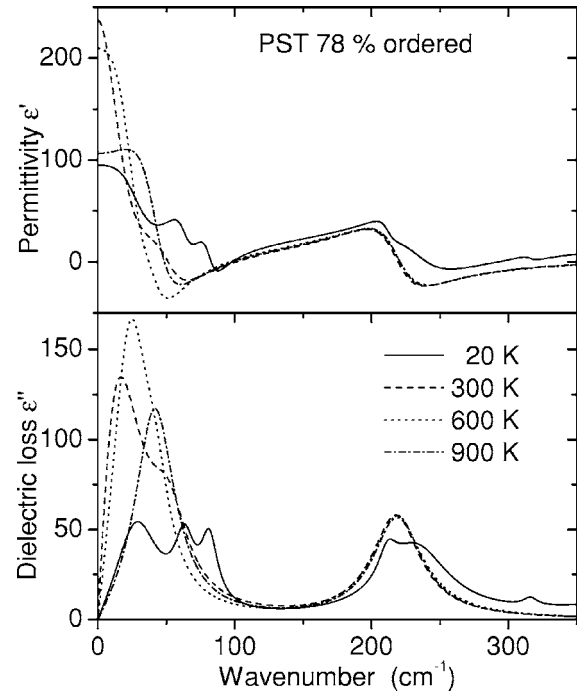


FIG. 2. Dielectric spectra of 78% ordered PST film obtained from the fit of transmission spectra for various temperatures.

well to parameters obtained from the bulk IR reflectivity spectra published in Ref. 21. It shows that the phonon parameters are not influenced by a possible strain or size effect in our thin films. We believe that the IR transmission spectra are more sensitive than the IR reflectivity spectra. It could be the reason why we could see also the splitting of the  $\text{TO}_2$  mode although it was not resolved in the IR reflectivity spectra.

The most important mode anomalies were observed in the range below  $100\text{ cm}^{-1}$ . Temperature dependences of the polar mode frequencies are plotted in Fig. 3. A new heavily damped (i.e.,  $\gamma_j/\omega_j > 1$ ) excitation appears on cooling below 700 K at frequencies near  $30\text{ cm}^{-1}$ . This mode is not manifested by a minimum in the IR transmission spectra, but rather by enhanced broad absorption below  $40\text{ cm}^{-1}$ . This

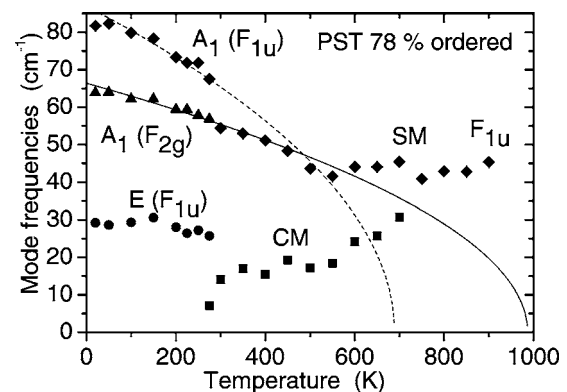


FIG. 3. Temperature dependences of the polar mode frequencies in 78% ordered film. The lowest-frequency mode below  $30\text{ cm}^{-1}$  (marked as CM) is overdamped, therefore the frequency of loss maximum corresponding to  $\omega_{\text{CM}}^2/\gamma_{\text{CM}}$  is plotted. Two kinds of the Cochran fit of the SM (shown by solid and dashed lines) are discussed in the text.

excitation does not seem to be of usual one-phonon origin, and we assign it to dynamics of polar clusters (i.e., CM).

Disappearance of the CM above 700 K is manifested by an enhancement of the low-frequency transmission, although the high-frequency transmission continues to decrease on heating, as expected due to increase of multiphonon absorptions and damping of polar phonons (see Fig. 1). On cooling to  $T_c \approx 300$  K, CM slows down to microwave range and vanishes below  $T_c$  from our spectral range.

Another heavily damped excitation arises in our IR spectra below  $T_c$  near  $30\text{ cm}^{-1}$  and remains in the spectra down to the lowest temperatures. The origin of this excitation was not fully understood until recently (in analogy to PMN, where it also appears,<sup>8</sup> it could be explained by the activation of the acoustic-phonon branches due to the local unit-cell doubling or translation symmetry breaking). However, now it seems to us more probable that it is just the  $E$  component of the split  $F_{1u}$  SM (for this explanation see below).

Let us stress that our static permittivity in Fig. 2 does not correspond to experimental low-frequency permittivity, because strong dielectric dispersion exists below the phonon frequencies.<sup>11</sup> Bovtun *et al.* combined the high-frequency and microwave dielectric spectra of PST ceramics between 1 MHz and 36 GHz (Ref. 11) with the IR reflectivity spectra<sup>21</sup> and revealed two dispersion regions below phonons. One, nearly temperature independent, was estimated to near 1 THz and corresponds well to our heavily damped mode near  $30\text{ cm}^{-1}$  below  $T_c$ . Second relaxation was seen at temperatures below 350 K in the high-frequency range and it slows down and broadens on cooling. At higher temperatures it merges with the far IR spectra so that it corresponds to the relaxation below  $T_d$  near  $30\text{ cm}^{-1}$  assigned to the dynamics of polar nanoclusters. This relaxation is responsible for the pronounced dielectric anomaly near and above  $T_c$ . The relaxation does not completely vanish at low temperatures, because our dielectric data at 1 MHz and 8 GHz obtained on PST thin films of various  $B$ -site order show permittivity between 300 and 400 at 20 K,<sup>24</sup> whereas the phonon contribution to permittivity is only about 100 (see Fig. 2). This is not surprising because a small dielectric dispersion (constant dielectric losses) was observed in many relaxors at low temperatures.<sup>5,6</sup>

The lowest-frequency phonon (marked  $\text{TO}_1$ ) with the symmetry  $F_{1u}$  has the frequency near  $45\text{ cm}^{-1}$  at high temperatures. It starts to harden below 550 K and it seems to split below  $T_c$ . For illustration, in Fig. 3 we fitted the temperature dependences of both components by the Cochran law, but rather different extrapolated critical temperatures (700 and 1000 K, respectively) were obtained. Although the realistic value could be somewhere in between, the softening ceased near 600 K and above the Burns temperature of about 700 K the expected hardening is not appreciable.

Both components of the  $\text{TO}_1$  SM have their counterparts in the Raman spectra,<sup>17</sup> but the assignment of the modes in Raman spectra is more speculative. One mode near  $56\text{ cm}^{-1}$  dominates the Raman spectrum below  $100\text{ cm}^{-1}$  in the paraelectric phase.<sup>17</sup> If we assume that it is Raman active due to  $B$ -site ordering, it should be of the  $F_{2g}$  symmetry, stemming from the Brillouin zone boundary of simple cubic per-

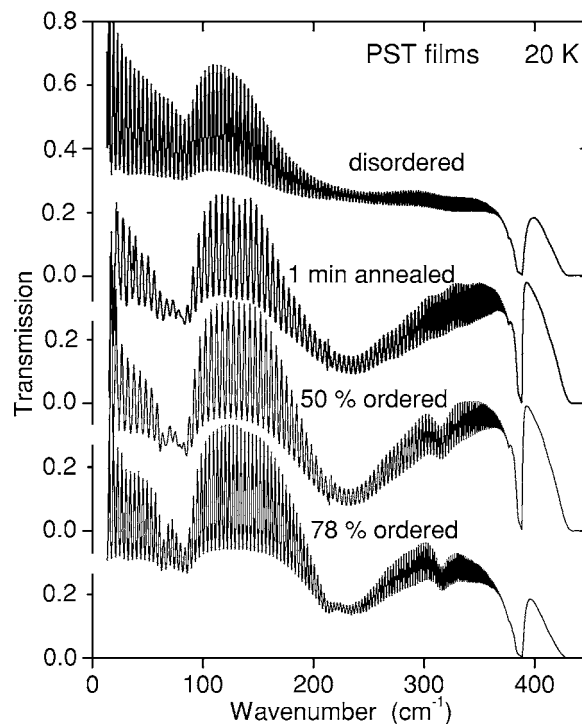


FIG. 4. Low-temperature IR transmission spectra of PST films with various  $B$ -site order.

ovskite structure. Its frequency is about  $10\text{ cm}^{-1}$  higher than that of the  $F_{1u}$  mode in our IR spectra (Fig. 3). At low temperatures a triplet appears in the Raman spectra with frequencies about 50, 60 (strong peak), and  $80\text{ cm}^{-1}$  (at 100 K).<sup>17</sup> The mode near  $80\text{ cm}^{-1}$  corresponds to the  $A_1$  component of our  $\text{TO}_1$  SM, which may activate in the Raman spectra below  $T_c$ . The mode near  $50\text{ cm}^{-1}$  could be assigned to the  $E$  component of the cubic  $F_{2g}$  mode and is seen only in the Raman spectra, although it could be also (weakly) IR active. The mode near  $60\text{ cm}^{-1}$  wavenumbers could correspond to the  $E$  component of the  $\text{TO}_1$  SM (see Fig. 3) or to the  $A_1$  mode from the split  $F_{2g}$  mode. The latter explanation is more realistic because this mode is the strongest one in the Raman spectra, and its strength decreases in the IR spectra with increasing disorder at the  $B$ -sites (see Fig. 4). This would mean that the mode near  $30\text{ cm}^{-1}$  should be assigned to the  $E$  component of the polar SM ( $F_{1u}$ ). This mode should remain IR active up to 700 K due to the dielectric anisotropy in polar clusters,<sup>27</sup> but it is probably screened by the CM at high temperatures. This assignment sheds a new light on softening of both modes near 80 and  $60\text{ cm}^{-1}$ . The higher-frequency mode softens, and because both modes are of the same  $A_1$  symmetry they can bilinearly couple which results also in the partial softening of the lower-frequency mode due to the mode repulsion.

Let us discuss the question of how the polar-phonon parameters in PST are influenced by the different  $B$ -site ordering. The difference is best remarkable at 20 K, where the phonon damping is minimized and the phonons up to  $400\text{ cm}^{-1}$  can be resolved in our IR spectra. Transmission spectra of four PST films with various order are compared at 20 K in Fig. 4. One can see that the  $\text{TO}_2$  splitting (two minima near  $230\text{ cm}^{-1}$ ) is appreciable only in the highest

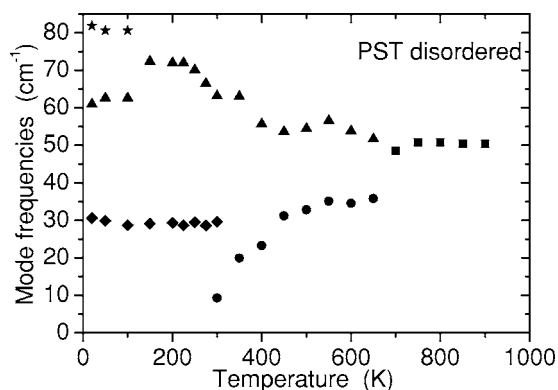


FIG. 5. Temperature dependences of the polar mode frequencies in disordered PST film.

ordered film.  $TO_1$  splitting below  $100\text{ cm}^{-1}$  is less and less pronounced with the decrease in ordering, but mostly due to the increase in the linewidths.

Let us note that the film annealed at  $850\text{ }^\circ\text{C}$  for 1 min does not show any ordering in x-ray diffraction (XRD),<sup>24</sup> however, remarkable difference between the disordered and 1 min ordered film is seen in our IR spectra. It shows that some short-range ordering occurs already in the 1 min annealed film, but XRD is not sensitive enough to see it.

Reaney *et al.*<sup>20</sup> correlated the intensity of Sc-Ta stretching mode in PST seen at  $315\text{ cm}^{-1}$  with the degree of B-site order. One can see this mode clearly in 50% and 78% ordered films, in the other two samples only a weak shoulder appears (Fig. 4). Unfortunately, we cannot establish any quantitative correlation between the intensity of this mode and the degree of order. Namely, the spectra of 78% ordered and disordered films were measured on substrates which were not polished on the bottom surface, while the other two substrates were well polished on both surfaces. Matted bottom surface causes parasitic diffuse scattering of the IR beam at higher frequencies which is responsible for the lower value of the transmission peak at  $400\text{ cm}^{-1}$  in the corresponding film spectra. Fortunately, the quality of the rear substrate surface has no influence on our spectra below  $200\text{ cm}^{-1}$  because the IR beam with a wavelength larger than  $50\text{ }\mu\text{m}$  does not feel its roughness.

Temperature dependences of the mode frequencies in disordered PST film are plotted in Fig. 5. The mode near  $60\text{ cm}^{-1}$  appears only below  $100\text{ K}$  due to the line broadening compared to the ordered film. Its lower strength than in the ordered sample gives evidence that it is the  $A_1$  component of the  $F_{2g}$  Raman mode. The  $A_1$  component of the  $TO_1$  SM exhibits behavior similar to that in the 78% ordered film: it softens on heating towards the Burns temperature which ceases above  $700\text{ K}$ . CM appears below  $650\text{ K}$  and slows down below our spectral range on cooling. The new heavily damped mode (probably the  $E$  component of the  $F_{1u}$  SM) appears below  $T_c$  at  $30\text{ cm}^{-1}$ . This mode was observed in all studied PST films as well as in the PMN film.<sup>8</sup> In Ref. 8 we suggested that the overdamping of the SM in the inelastic neutron scattering spectra of PMN (so-called “waterfall” effect) is only an apparent effect. We suggested that the SM were underdamped (as in IR spectra) but disappeared from

the neutron spectra due to its overlapping with the CM which approached the terahertz range near  $T_d$ . The SM and CM behavior in PMN and PST is therefore very similar, but PST was not studied by inelastic neutron scattering so that no similar comparison is possible.

## V. CONCLUSION

In conclusion, our IR transmission spectra of variously ordered PST thin films show qualitatively the same behavior: soft  $TO_1$  phonon of  $F_{1u}$  symmetry splits on cooling below the Burns temperature.  $A_1$  component hardens and follows the Cochran law with extrapolated critical temperature slightly above the Burns temperature. The low-frequency  $E$  component is clearly seen at low temperatures, but it is probably active up to  $T_d$ , where it is screened by the overdamped CM with similar frequency. CM stemming from dynamics of polar clusters appears below the Burns temperature and slows down to  $T_c$ . Similar behavior was observed also in the PMN relaxor,<sup>8</sup> so it seems that such a phonon and CM behavior is general for most perovskite relaxor ferroelectrics.

## ACKNOWLEDGMENTS

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