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## **Soft-mode spectroscopy of ferroelectrics and multiferroics**

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Fyzika kondenzovaných systémů

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## 1. Introduction

Let us start first with a short historical remark. The concept of FE soft mode, i.e. one or several polar phonons, whose frequency tends to zero or greatly decrease near the temperature of structural PT  $T_c$ , is very old and it is frequently used for explanation of dynamics of the PTs. Classical Cochran's papers<sup>1,2,3</sup> from 1959-1961 are usually considered as the first papers about this topic, but Anderson<sup>4</sup> came with the idea of soft mode already in 1958. He published his paper only in Russian and although the paper appeared only in conference proceeding two years later,<sup>4</sup> it is rather frequently cited in Eastern Europe. Nevertheless, one must accept, that the first original ideas about the FE soft mode were published by Ginzburg already in 1949,<sup>5,6,7</sup> but at that period the Russian papers were not translated to English, therefore these articles were forgotten.

First observation of the soft mode is even older. Landsberg and Mandelstam<sup>8</sup> saw some soft mode in Raman spectra near the  $\alpha \leftrightarrow \beta$  transition in quartz already in 1929, but they explained its temperature behaviour inaccurately. Therefore the papers of Barker and Tinkham,<sup>9</sup> as well as of Cowley<sup>10</sup> published in 1962, are considered as the first papers, which experimentally confirmed the soft mode theory. Let us note that both papers concern the study of quantum paraelectric SrTiO<sub>3</sub> above 90 K. By the way, most of experimental works in 1960's refer to soft mode studies of quantum paraelectrics SrTiO<sub>3</sub> and KTaO<sub>3</sub> probably due to the relatively high soft mode frequency and large temperature changes observed in these materials. Regarding the experimental techniques, mostly inelastic neutron scattering and Raman scattering were used. Far infrared (IR) spectroscopy was less used, but it became to be more popular in the 1970's with the development of fast Fourier spectroscopy. Nevertheless, this technique is more appropriate than other techniques, because the soft mode is IR active in both paraelectric and FE phase, in contrast to Raman scattering, where the soft mode is mostly active only in the FE phase or it can be activated in paraelectric phase by an external electric field. Inelastic neutron scattering has the advantage that it allows to measure dispersion of the soft optical phonon branch in the whole Brillouin zone, but this measurement is much more time consuming, matchlessly more expensive and moreover large single crystals are needed for such experiments.

In the beginning of 1970's, the soft mode spectroscopy was used already frequently for the study of dynamics of phase transitions – see the review papers<sup>11,12</sup> and a monography<sup>13</sup>. It was shown that the optical soft mode is a dynamical origin of only displacive structural PTs. In the case of order-disorder PTs (see below), the soft mode is not an optical phonon, but it has a

relaxational character and slowing down of the relaxation frequency is seen in microwave (MW), radio- or low-frequency ranges on cooling towards  $T_c$ .<sup>12</sup>

Our laboratory in the Institute of Physics, Czech Academy of Sciences, has a long tradition in investigation of the FE soft modes thanks to J. Petzelt, who was active in this field since 1966. In 1983 the laboratory was equipped with a new Fourier Transform spectrometer Bruker IFS 113v (equipped with He-cooled bolometer) and in the same time I started my diploma work with this instrument. The work dealt with a far IR investigation of phonons near the incommensurate PT in BaMnF<sub>4</sub>.<sup>14</sup> Later on, I wrote my PhD thesis in the same lab. The work was devoted to the investigation of lattice dynamics in highly anharmonic KSCN crystal with an order-disorder PT,<sup>15</sup> to betaine calcium chloride dehydrate<sup>16,17</sup> (organic material with a sequence of 16 PT's to various commensurately and incommensurately modulated phases) as well as to high-temperature superconductors.<sup>18,19</sup> In the beginning of 1990's, I was lucky to spend a longer stay at the ETH Zurich and at the University of Würzburg continuing in the field of IR studies of various ferroelectrics, in the latter case even with the help of high hydrostatic pressure. After my return back in 1995, our Prague lab was gradually developed with a new equipment (Raman and micro-Raman spectrometers, two impedance analysers covering the frequency range of 0.1 Hz – 1.8 GHz, network analyzer (50 MHz – 50 GHz) and mainly P. Kužel developed a time-domain THz spectrometer (100 GHz – 2.5 THz) based on a laser with ultrashort femtosecond pulses. All these instruments allowed us to cover practically continuously the spectral range from 0.1 Hz up to 150 THz. Moreover, most of the measurements are possible to be carried out in a broad temperature range 5 - 900 K. Such a unique equipment ranks our lab in the front of world laboratories working in the field of dielectric spectroscopy.

Demand of miniaturization of the new capacitors in integrated circuits requires new dielectric materials with high permittivity. In the case of non-volatile memories the capacitors or transistor gates should be moreover FE. However, the permittivity in ceramics and thin films is markedly reduced compared to the single crystals due to the low-permittivity grain boundaries, dead layers between the thin films and substrates, as well as due to the strain in the films caused by a misfit between the substrates and films.<sup>20</sup> Understanding the permittivity reduction is necessary for processing good quality thin films and ceramics and broad-band dielectric spectroscopy helps a lot in this case.

In the 1990's a giant piezoelectric effect was revealed in FE relaxor-based single crystals, which allowed construction of new and much more efficient piezoelectric devices. Since that time the interest in relaxors rapidly increased and mainly the broad-band dielectric spectroscopy

(including of our works) contributed a lot in understanding of the mechanisms of giant piezoelectric effect and structural PTs in these materials.

Within the last 25 years we investigated dynamics of structural PTs in many FE materials, which allowed us to generalize the soft mode behaviour: In reality the SM never softens completely, some finite frequency can be observed at  $T_c$ . Several reasons can be given for the softening saturation:<sup>21</sup>

- First-order nature of the structural PT.
- Quantum effects at low temperatures in incipient ferroelectrics.
- Polar soft mode is not the critical soft mode of the PT. The proper soft mode is coming from outside of the Brillouin zone centre. This is the case of antiferroelectric PT's, incommensurate FE transitions or improper FE PTs.
- The most frequent case is that the central mode type dispersion (in other words, a dielectric relaxation) appears near  $T_c$  below the optical SM frequency. Both modes are coupled and the central mode is mainly responsible for the dielectric anomaly near  $T_c$ . This case occurs due to defects or more often at the crossover from the displacive to order-disorder type PTs.

In this work we will review results mostly from the last 25 years.

## 2. Scientific background

In usual proper ferroelectrics, the low-frequency permittivity above the second order PT temperature  $T_c$  follows the Curie-Weiss law<sup>13</sup>

$$\varepsilon' = \frac{C}{(T-T_c)} \quad (1)$$

where  $C$  is the Curie-Weiss constant. The complex permittivity  $\varepsilon^* = \varepsilon' + i\varepsilon''$  is determined by a sum of contributions of the high-frequency electronic polarization ( $\varepsilon_\infty$ ), polar phonons ( $\varepsilon_{ph}$ ) and possibly of some dielectric relaxations ( $\varepsilon_{dr}$ ), which can be usually expressed as a sum of damped harmonic oscillators and Debye relaxations:<sup>13</sup>

$$\varepsilon^*(\omega) = \varepsilon_\infty + \varepsilon_{ph} + \varepsilon_{dr} = \varepsilon_\infty + \sum_j^n \frac{\Delta\varepsilon_j \omega_{TOj}^2}{\omega_{TOj}^2 - \omega^2 + i\omega\gamma_j} + \sum_j^m \frac{\Delta\varepsilon_{Rj} \omega_{Rj}}{\omega_{Rj} + i\omega} . \quad (2)$$

$\omega_{TOj}$ ,  $\gamma_j$  and  $\Delta\varepsilon_j$  denote the transverse frequency, damping and dielectric contribution to the static permittivity of the  $j$ -th polar phonon, respectively, and  $\Delta\varepsilon_{Rj}$  and  $\omega_{Rj}$  mark the dielectric strength and relaxation frequency of the  $j$ -th relaxation, respectively. In the case of displacive PTs, the relaxation contribution  $\varepsilon_{dr}$  should be zero in the paraelectric phase and the increase in

permittivity near  $T_c$  (see Eq. 1) is caused by softening (i.e. decrease of the frequency) of one of the polar phonons. If the phonons are not coupled, the oscillator strengths  $f_j = \Delta\varepsilon_j \omega_{\text{TO}j}^2$  of all polar modes are expected to be roughly temperature independent. It means, for example, that if the soft mode frequency  $\omega_{\text{SM}}$  reduces twice,  $\Delta\varepsilon_{\text{SM}}$  increases four times, etc. Temperature dependence of the  $\omega_{\text{SM}}$  can be easily obtained from the Curie-Weiss law (Eq. 1) and Lyddane-Sachs-Teller relation,<sup>22</sup> which expresses the relation between static permittivity  $\varepsilon_0$  and high frequency permittivity  $\varepsilon_\infty$  with longitudinal  $\omega_{\text{LO}}$  and transverse  $\omega_{\text{TO}}$  phonon frequencies. For materials with two atoms per unit cell, it has the form<sup>22</sup>

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \frac{\omega_{\text{LO}}^2}{\omega_{\text{TO}}^2}. \quad (3)$$

$\varepsilon_\infty$  and  $\omega_{\text{LO}}$  are usually only slightly temperature dependent and because  $\varepsilon_0$  diverges at  $T_c$  (see Eq. 1), transverse phonon frequency  $\omega_{\text{TO}}$  should decrease to zero at  $T_c$ . If we assume  $\varepsilon_\infty$  and  $\omega_{\text{LO}}$  constant and if we put  $\omega_{\text{TO}} = \omega_{\text{SM}}$ , we obtain Cochran law for the temperature dependence of the soft mode frequency<sup>1</sup>

$$\omega_{\text{SM}}^2 = A(T - T_c) \quad (4)$$

where  $A$  is the Cochran constant. For materials with more atoms per unit cell, the generalized Lyddane-Sachs-Teller relation has the form<sup>13</sup>

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \prod_{j=1}^n \frac{\omega_{\text{LO}j}^2}{\omega_{\text{TO}j}^2}. \quad (5)$$

In the case of non-coupled phonons only one transverse phonon frequency is temperature dependent and one can obtain again the Cochran law (Eq. 4). Although the concept of the optical soft mode as the dynamical origin of the PT is accepted since 1960, there are only several pure displacive ferroelectrics known (e.g.  $\text{PbTiO}_3$ <sup>23</sup>), where the low-frequency dielectric anomaly is caused only by softening of the optical soft mode. Also for pure incipient ferroelectrics like  $\text{SrTiO}_3$ ,<sup>9,24,25</sup> and  $\text{KTaO}_3$ ,<sup>24,26</sup> where the soft mode does not soften completely, because the FE PT is not reached in these materials, the soft mode is completely responsible for the anomalous temperature dependence of the low-frequency permittivity.

If the high-temperature paraelectric structure is disordered, i.e. if some kind of atoms occupy two or more equivalent positions with the probability less than 1, the atoms usually order below  $T_c$  only in some of the mentioned sites and we say that the system undergoes an order-disorder phase transition at  $T_c$ . If the ordering of ions is connected with appearance of spontaneous polarization, the PT is FE. In this case the phonons may exhibit only small temperature

anomalies and the dynamical origin of the PT is the critical slowing-down of some relaxation frequency  $\omega_{Rj}$  (see the last term in Eq. 2) near  $T_c$ , which expresses the hopping motion of the disordered atoms among the equivalent positions in paraelectric phase. The soft relaxation frequency  $\omega_{Rs}$  in the disordered materials plays the role of the optical soft mode in displacive ferroelectrics and follows the simple linear temperature dependence above  $T_c$ <sup>12</sup>

$$\omega_{Rs} = A'(T - T_c). \quad (6)$$

Below  $T_c$  the soft dielectric relaxation usually disappears from the spectra, but another relaxation may appear due to dynamics of FE domain walls. If we take into account that the relaxation frequency cannot increase up to infinity on heating, we should add to the linear dependence (Eq. 6) some saturation frequency  $\omega_{sat}$ . Modified law for the soft relaxation frequency has than the form<sup>27</sup>

$$\omega_{Rs}^{-1} = [A'(T - T_c)]^{-1} + \omega_{sat}^{-1} \quad (7)$$

Relaxation strength  $f_{Rs} = \Delta\epsilon_{Rs}\omega_{Rs}$  of the soft relaxation in the paraelectric phase can be assumed temperature independent and due to the slowing down of  $\omega_{Rs}$  one can obtain the Curie-Weiss increase of the static permittivity. Typical examples of materials with order-disorder PT are KDP-type ferroelectrics, triglycine sulphate or sodium nitrite.<sup>12,13</sup>

Many materials were reported as classical displacive or order-disorder ferroelectrics, however their detailed investigations have shown that they usually exhibit some crossover between both kinds of mechanism of the PTs. For example, an underdamped optical soft mode was observed in the THz spectra of tris-sarcosine calcium chloride (TSCC),<sup>28</sup> therefore this material was assumed to be displacive FE. However, the careful reinvestigation of the THz spectra of TSCC and comparison with the low-frequency dielectric data revealed a soft relaxation (central mode) close to  $T_c$  which is responsible for critical deviations from the Curie-Weiss law and the Cochran law near  $T_c$ .<sup>29</sup> The central mode was assigned to critical polar cluster dynamics. On the other hand, also many ferroelectrics with order-disorder PTs show critical slowing down of the relaxation which is coupled with optical phonons or other higher-frequency relaxations. It means that the driving force of the PT is the latter excitation, although the dielectric anomaly near  $T_c$  is mainly due to the soft relaxation. As the examples Rochelle salt<sup>30</sup> or  $\text{LiNaGe}_4\text{O}_9$ <sup>27</sup> can be named, which will be here discussed, other examples can be found in the reviews.<sup>12,20,31</sup>

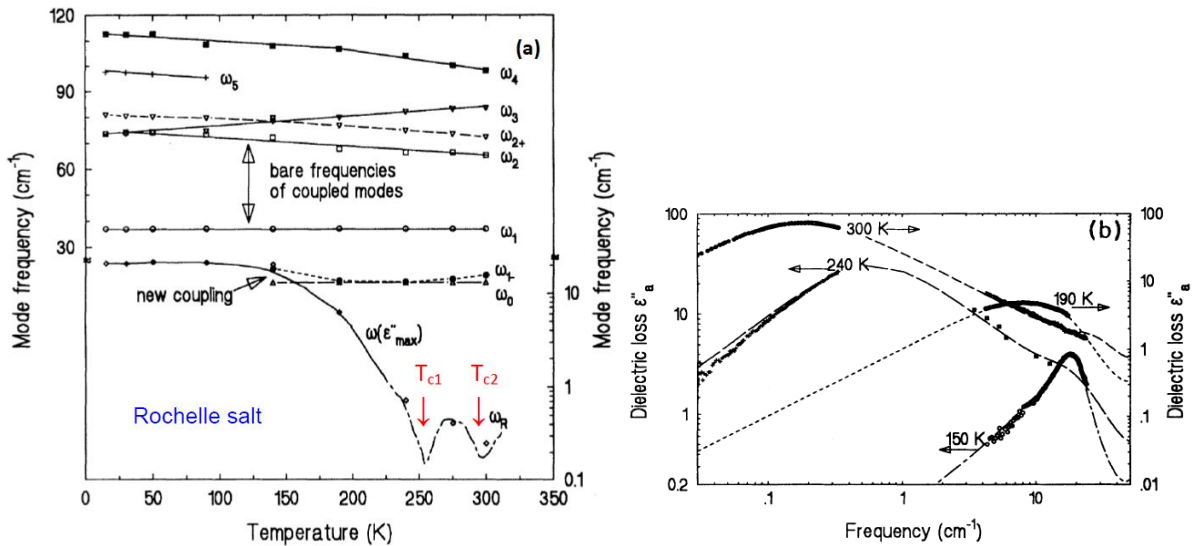
It seems nowadays that the PTs with a pure soft optical mode or a pure soft relaxation mode are rather rare. Most of materials exhibit crossover between displacive and order-disorder PT, i.e. the phonons exhibit anomalies near  $T_c$ , however their contributions to permittivity do not



explain the complete dielectric anomaly near  $T_c$ . Additional soft relaxation (i.e. central mode) frequently appears near  $T_c$  and only the sum of both contributions is responsible for the dielectric anomaly near  $T_c$ .

### 3. Investigation of tatrates – hydrogen bonded ferroelectrics

Sodium potassium tartrate tetrahydrate  $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , called Rochelle salt (RS), is the first known ferroelectrics. Joseph Valashek revealed a FE hysteresis loop in this compound already in 1920,<sup>32</sup> but published in detail in 1921.<sup>33</sup> Although RS was studied by many authors within the last 100 years, the understanding of the mechanism leading to the formation of a state with a spontaneous polarization was a long time puzzling. In contrast to all other ferroelectrics, its FE phase (monoclinic space group  $\text{P}2_1-\text{C}_2^2$ ,  $Z=4$ ) exists only between  $T_{C1}=255$  K and  $T_{C2}=297$  K. Above and below these temperatures, RS is paraelectric with the same orthorhombic space group  $\text{P}2_12_12-\text{D}_2^3$ ,  $Z=4$ . Older neutron diffraction data<sup>34</sup> showed that the whole tartrate and crystal water molecules are disordered in the paraelectric phase with a small disordering amplitude. Newer reinvestigation using synchrotron x-ray diffraction revealed a disorder of only K atoms and three water O atoms in the paraelectric phase, while the bonded H atoms in water are not disordered.<sup>35</sup> A Debye relaxation mode was observed in the MW region and its relaxation frequency linearly decreases with temperature near  $T_{C1}$  and  $T_{C2}$ ,<sup>36,37,38</sup> therefore the PTs in RS were regarded as classical examples of the order-disorder type.



**Fig. 1.** Left: Temperature dependence of the mode frequencies obtained from the fit of  $E||a$  polarized spectra with the coupled-oscillator model. Modes with the bare frequencies  $\omega_1$  and  $\omega_2$  are coupled below 140 K, while the modes with frequencies  $\omega_1$  and  $\omega_0$  are coupled at higher temperatures and this coupling induces a soft critical dielectric relaxation  $\omega_R$  near both  $T_{C1}$  and  $T_{C2}$ . b) Dielectric loss spectra  $\epsilon''_a$  obtained from the fits of experimental microwave<sup>39</sup> and THz<sup>40</sup> spectra. From Ref. 30.

However, later it was shown that at low temperatures the relaxation hardens to the THz range and remarkably underdamps, so that it has phonon (i.e. resonant) character.<sup>40</sup> Because its oscillator strength  $f_{SM} = \Delta\epsilon_{SM}\omega_{SM}^2$  is reduced on cooling below  $T_{C1}$  by one order of magnitude, Volkov et al.<sup>41</sup> suggested that this mode is probably linearly coupled with another optical phonon in the FIR range. It means that the transition is more likely displacive than order-disorder.

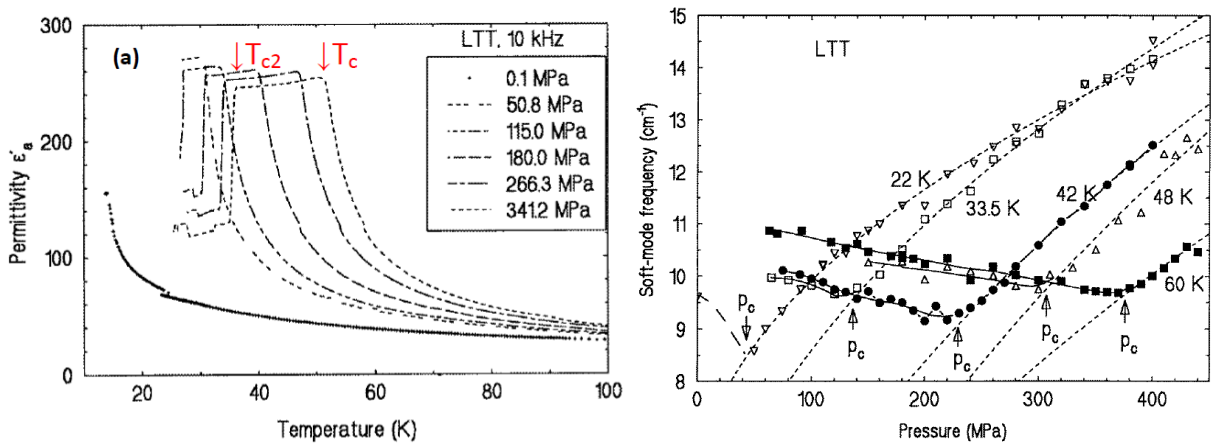
We have investigated the lattice dynamics of RS by means of IR, Raman and inelastic neutron scattering spectroscopies.<sup>30,42</sup> We have really observed the soft mode near  $20\text{ cm}^{-1}$  which is linearly coupled with the mode near  $75\text{ cm}^{-1}$  (see Fig. 1). The higher frequency mode partially softens on heating from low temperatures to  $T_{C1}$  and it causes the softening and rising damping of the mode near  $20\text{ cm}^{-1}$ . Moreover, the soft mode near  $20\text{ cm}^{-1}$  is coupled to an overdamped mode with temperature independent bare frequency  $13\text{ cm}^{-1}$ . Temperature dependent coupling of these modes causes critical slowing down of the dielectric relaxation, which is responsible for the strong dielectric anomalies seen near  $T_{C1}$  and  $T_{C2}$ . It means that the dynamical origin of the FE PTs in RS is not only a dielectric relaxation, but also unstable optical phonons near  $20$  and  $75\text{ cm}^{-1}$ . Therefore the PTs in RS can be treated as a mixture of displacive and order-disorder type.<sup>30</sup> This conclusion was also confirmed by IR measurements at high hydrostatic pressures, where we observed the largest influence of the pressure on the phonon of frequency near  $75\text{ cm}^{-1}$ ,<sup>43</sup> i. e. the mode which induces softening of the modes in THz and MW regions depicted in Fig. 1.

Chemically relative to RS is lithium thallium tartrate monohydrate (LTT) –  $\text{LiTlC}_4\text{H}_4\text{O}_6\cdot\text{H}_2\text{O}$ . It exhibits only one FE PT and its critical temperature  $T_c=11\text{ K}$  is one of the lowest known.<sup>44</sup> The free permittivity  $\epsilon'_a$  obeys the Curie-Weiss law well above  $T_c$ , but in contrast to other ferroelectrics,  $\epsilon'_a$  decreases only slightly below  $T_c$ .<sup>45</sup> The permittivity is very sensitive to the mechanical boundary condition, so whereas  $\epsilon'_a$  reaches  $\sim 5000$  at  $T_c$ , the clamped  $\epsilon'_a(T_c)$  is only  $\sim 30$ .<sup>46</sup> Both the elastic compliance at constant electric field  $s_{44}^E$  and the piezoelectric coefficient  $d_{14}$  become exceedingly large close to  $T_c$  (note that LTT is piezoelectric already in the paraelectric phase above  $T_c$ ) and appear to have the highest magnitude measured in any materials.<sup>46</sup>

The optical soft mode in LTT was first observed in far IR spectra by Gerbaux *et al.*<sup>47</sup> and investigated in more details by Volkov *et al.*<sup>48</sup> The latter authors have shown that its frequency

softens from  $21 \text{ cm}^{-1}$  at 300 K to  $9 \text{ cm}^{-1}$  at  $T_C$ , but its dielectric contribution  $\Delta\epsilon$  was two orders of magnitude smaller than the observed free permittivity near  $T_C$ . Therefore Volkov *et al.*<sup>48</sup> claimed that another dispersion of the relaxation type should exist in the MW region and the PT is of mixed displacive and order-disorder type. Nevertheless, Hayashi *et al.*<sup>49</sup> have shown that the free  $\epsilon'_a$  is enhanced due to piezoelectric resonances in the MW region and that the high frequency permittivity corresponds very well to the THz  $\epsilon'_a(T)$ .<sup>48</sup> Therefore the PT is purely displacive, although the optical soft mode does not soften completely due to its strong coupling with a transverse acoustic mode.

Piezoelectric paraelectric phase has an orthorhombic structure ( $P2_12_12 - D_2^3, Z=4$ ),<sup>50,51</sup> but the structure of FE phase was not known. Therefore we performed a new IR, Raman, dielectric and structural measurements of LTT. From the high-pressure dielectric data we have shown that  $T_C$  strongly increases with hydrostatic pressure (up to 54 K at 370 MPa).<sup>52</sup> Permittivity  $\epsilon'_a(T)$  exhibits an unusual plateau below  $T_C$  and then drops down in dependence on pressure by 5-15 K below  $T_C$  (Fig. 2). FE hysteresis loops are only slim in the range of plateau, giving evidence about easy movement of domain walls, but below the temperature of the drop down ( $T_{C2}$ ) the domains are frozen and the sample cannot be switched. The unusual temperature independence of  $\epsilon'_a$  seen between  $T_C$  and  $T_{C2}$  was theoretically explained by Tagantsev with a bilinear coupling between the order parameter (soft mode) and strain.<sup>53</sup> The optical soft mode is strongly temperature and pressure dependent. It exhibits minimum frequency at  $T_c$  but no anomaly near  $T_{C2}$ ,<sup>52</sup> i.e. no structural change occurs at  $T_{C2}$ , only the coupling between the soft mode and strains changes. We performed also an elastic neutron scattering experiment at hydrostatic pressure



**Fig. 2.** Left: Temperature dependence of the permittivity  $\epsilon'_a$  of LTT at various pressures. Right: Pressure dependence of the soft-mode frequencies at different temperatures obtained from the Raman b(cb)c spectra. The broken curves in the high-pressure FE phase are results of the square-root fits (equivalent to the Cochran law as a function of pressure). From Ref. 52.

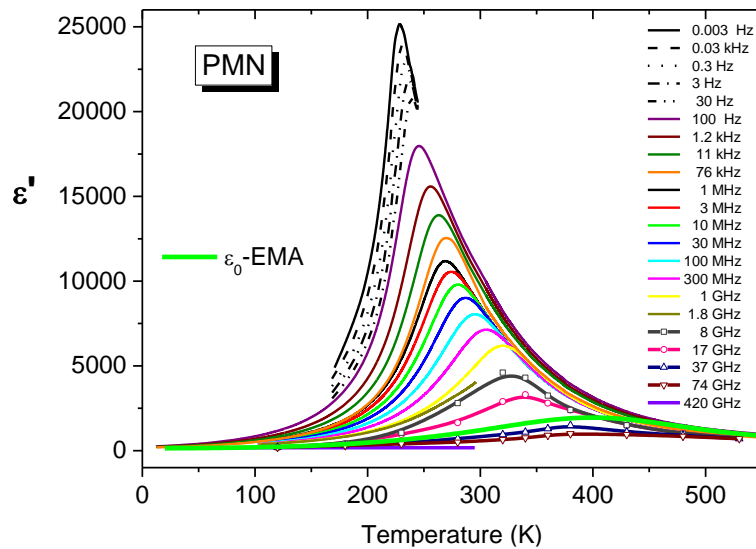
of 120 MPa with the purpose to determine symmetry of the FE phase.<sup>54</sup> We obtained monoclinic FE structure with a symmetry  $P2_111$  below both  $T_C$  and  $T_{C2}$ , with a larger monoclinic distortion below  $T_{C2}$  than below  $T_C$ .

Chemically related to LTT is lithium ammonium tartrate monohydrate (LAT). It exhibits the FE and ferroelastic PTs at  $T_c=98$  K. We investigated IR and Raman spectra of the LAT down to 15 K and no soft mode was observed,<sup>55</sup> because the PT is proper ferroelastic and improper FE. In contrast to LTT where a substantial increase of  $T_c$  with hydrostatic pressure was observed, in case of the LAT crystal  $T_c$  decreases only slightly down to 91 K at 400 MPa.<sup>55</sup>

#### 4. Lead-based relaxor ferroelectrics

Unlike classic ferroelectrics which exhibit a peak in permittivity  $\epsilon'(T)$  at the temperature of PT, which is frequency independent in displacive ferroelectrics or its height depends on frequency, but its temperature  $T_C$  does not change (in case of order-disorder PTs), there is another class of materials, which exhibits a high and frequency dependent peak in  $\epsilon'(T)$  – see e.g. Fig. 3. These materials frequently do not exhibit any FE PT without external electric field, but since they show many similarities with ferroelectrics, they are called relaxor ferroelectrics.

Since the discovery of the first relaxor FE  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) by Smolenskii and Agranovskaya<sup>56</sup> in the end of 1950<sup>th</sup>, many materials with similar dielectric properties were found. Isupov<sup>57</sup> tried to explain the peculiar dielectric anomaly in relaxors by a diffuse PT, i.e. by a distribution of the FE PT temperatures due to microscopic inhomogeneities in the samples. Nevertheless, later it was shown that the relaxor dielectric anomaly is not necessary caused by



**Fig. 3.** Temperature dependence of permittivity in relaxor FE  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  depicted at various frequencies.  $\epsilon_0$ -EMA curve is result of calculation of the phonon static  $\epsilon_0$  using effective medium approximation described in Ref. 82. Modified after Ref. 79.

a PT. For example, model relaxor FE PMN exhibits non-polar cubic structure down to liquid helium temperatures<sup>58</sup> and it becomes FE only under cooling in bias electric field.<sup>59</sup> In 1983 Burns and Dacol measured temperature dependences of the optical refractive index in various relaxors and observed a deviation from the linear temperature dependence some 300 K above the temperature  $T_m$ , where  $\epsilon'(T)$  shows maximum.<sup>60</sup> They explained it by a creation of polar clusters and since that time the temperature  $T_d$  is called the Burns temperature. Nowadays it is believed that most of peculiar physical properties of relaxors are somehow connected with the polar nanoclusters, which appear probably due to some quenched random electric fields<sup>61</sup> from cations of different valences, which are sitting in the equivalent perovskite sites (e.g.  $Mg^{2+}$  and  $Nb^{5+}$  in PMN), however details are still not fully understood.

In 1997 Park and Shrout<sup>62</sup> showed that relaxor-based  $PbMg_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$  (PMN-PT) and  $PbZn_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$  (PZN-PT) single crystals exhibit ultrahigh strain and piezoelectric behaviour in electric field, and since that time the interest for relaxors rapidly increased, because these materials show many technical applications in piezoelectric devices and microelectronics. Besides many research papers published on relaxors, also several reviews appeared. We can refer the reader to reviews of Cross,<sup>63,64</sup> Ye,<sup>65</sup> Samara,<sup>66,67</sup> Bokov,<sup>68,69</sup> where the present knowledge of relaxors is overviewed. There are also several reviews about the lattice dynamics of relaxors. Results of Raman scattering were reviewed by Siny et al.<sup>70</sup>, inelastic neutron scattering results by Shirane and Gehring<sup>71</sup> and Cowley et al.<sup>72</sup> IR and MW dielectric dispersion by Kamba and Petzelt,<sup>73</sup> Hlinka et al.<sup>74</sup> and Buixaderas et al.<sup>31</sup>

We have demonstrated that for understanding of peculiar dielectric dispersion in relaxors a broad-band dielectric spectroscopy from sub-Hz up to THz and IR frequencies is necessary. First of all, we investigated ceramics of lanthanum modified lead zirconate titanate  $(Pb_{1-x}La_x)(Zr_yTi_{1-y})_{1-x/4}O_3$  (PLZT 100(x/y/1-y)) with  $x = 8$  and  $9.5$  and  $y = 65$ .<sup>75</sup> Both ceramics exhibit a broad and strongly frequency dependent peaks in  $\epsilon'(T)$  and  $\epsilon''(T)$  seen between 325 K (at 100 Hz) and 500 K (at 36 GHz). A single broad and symmetric dispersion that occurs below the polar phonon frequencies, was fitted with the Cole-Cole formula and with the uniform distribution of Debye relaxations. On decreasing temperature, the distribution of relaxation times becomes extremely broad (10 orders of magnitude at 300 K in PLZT 9.5/65/35 - see Fig. 4 left) which indicates increasing correlation among the clusters. The mean ( $\tau_0$ ) and upper ( $\tau_1$ ) relaxation times diverge according to the Vogel-Fulcher law<sup>75</sup>

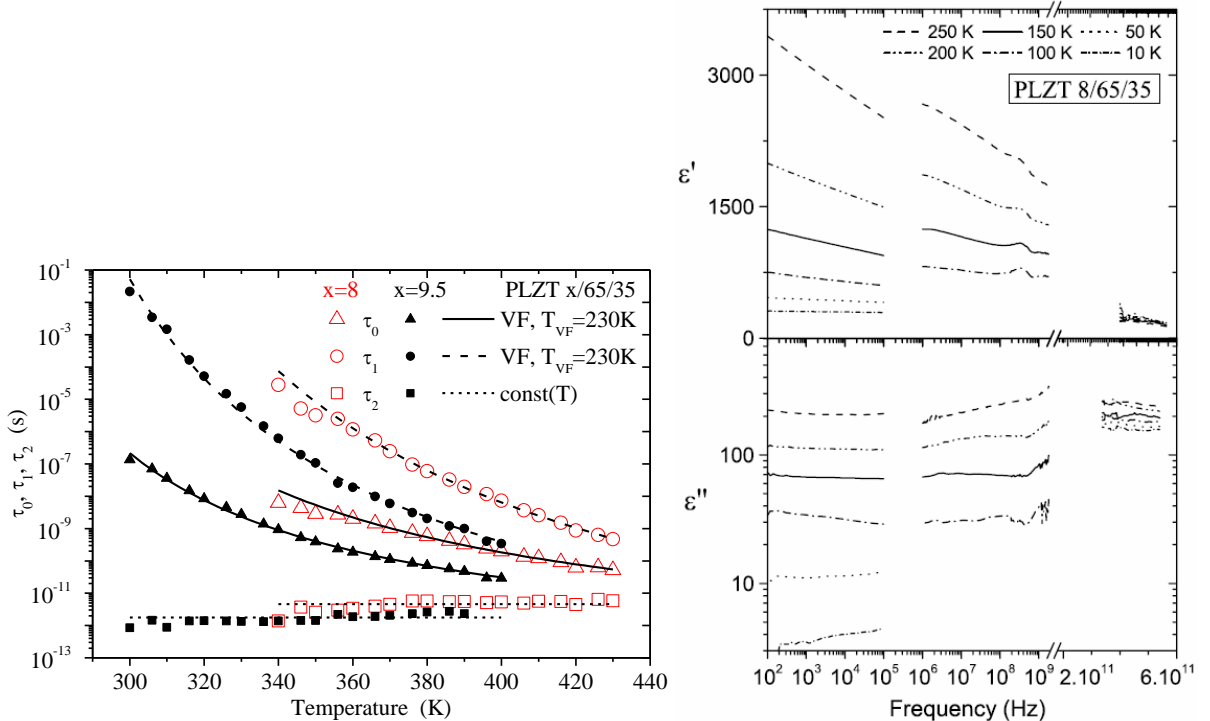
$$\tau_{0,1}(T) = \tau_L \exp\left(\frac{U_{VF}}{T-T_{VF}}\right) \quad (8)$$

with the same freezing temperature  $T_{VF} = 230 \pm 5$  K for both ceramics, but different activation energies  $U_{VF}$  1370 K and 1040 K for the PLZT 8/65/35 and 9.5/65/35, respectively.  $\tau_L$  in Eq. (1) marks the limiting high-temperature relaxation time, which is of the order of the reciprocal lowest optical phonon frequency. The shortest relaxation time  $\tau_2$  is about  $10^{-12}$  s and remains almost temperature independent (Fig. 4 left). Below room temperature, the loss spectra  $\varepsilon''(\omega)$  become essentially frequency independent and the permittivity increases linearly with decreasing logarithm of frequency (Fig. 4 right).<sup>76</sup> This behaviour was successfully explained by a constant distribution  $g(\tau)$  of equally strong Debye relaxations between upper ( $\tau_1$ ) and lower ( $\tau_2$ ) limits of relaxation times. We have shown that if the measured frequency range is much narrower than the distribution  $g(\tau)$ , the complex permittivity can be expressed as:<sup>75</sup>

$$\varepsilon'(\omega) = \varepsilon_\infty - B(T) \ln(\omega\tau_2) \quad (9)$$

$$\varepsilon''(\omega) = \frac{\pi}{2} B(T)$$

where  $B(T)$  is the frequency-independent but temperature-dependent parameter describing the magnitude of  $g(\tau)$ . This model was successfully used not only for description of the low-temperature dielectric properties of relaxor PLZT<sup>75</sup> (Fig. 4 right), PMN<sup>79</sup> and  $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$

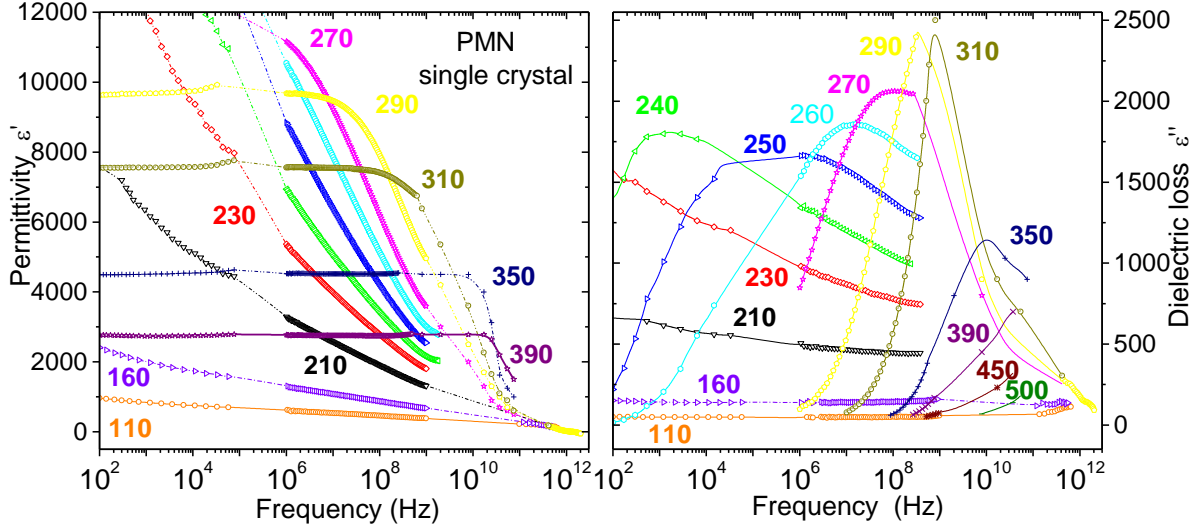


**Fig 4.** Left: Temperature dependence of the mean ( $\tau_0$ ), upper ( $\tau_1$ ) and lower ( $\tau_2$ ) relaxation times in relaxor PLZT determined from the uniform distribution model of Debye relaxation frequencies. Right: Frequency dependence of the real and imaginary parts of the complex permittivity in PLZT 8/65-35 at various temperatures close and below freezing temperature  $T_{VF}$ . After Refs. 75 and 76.

(PMT),<sup>77</sup> but also for fitting of the anomalous broad dielectric relaxation in  $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$  with cubic pyrochlore structure,<sup>78</sup> which is not a relaxor FE. In this case the upper relaxation time follows the Arrhenius law and the relaxation was assigned to the local hopping of atoms in the A and O' positions of the pyrochlore structure among several local potential minima.

The archetypical and best-studied relaxor FE is PMN because its solid solution with  $\text{PbTiO}_3$  is material with the highest piezoelectric coefficients. Typical relaxor peak in  $\epsilon'(T)$  measured between 3 mHz and 420 GHz is shown in Fig. 3.<sup>79</sup> Frequency plots of the dielectric function (Fig. 5) reveal similar behavior as in PLZT: a slowing down and broadening of the dielectric relaxation on cooling.<sup>80</sup> Again, in the logarithmic scale linearly dependent  $\epsilon'(\omega)$  and frequency independent loss spectra  $\epsilon''(\omega)$  are seen below the freezing temperature  $T_{\text{VF}} \cong 230$  K. Qualitatively similar dielectric behavior was observed in all relaxors and we interpreted it as follows:<sup>81</sup> The dielectric relaxation appears in the spectra below the Burns temperature ( $T_{\text{d}} = 600 - 700$  K in various relaxors) and expresses a dynamical flipping of the cluster polarization. Below the freezing temperature  $T_{\text{VF}}$  the clusters freeze out and the flipping of polarization disappears. Nevertheless, the polar cluster boundaries can still vibrate (breeze) below  $T_{\text{VF}}$ , but since it is a temperature activated process over energy barriers with some distribution, the relaxation times (or frequencies) exhibit also a distribution  $g(\tau)$ , which broadens on cooling. This low-temperature  $g(\tau)$  is responsible for the dielectric dispersion observed below  $T_{\text{VF}}$  (e.g. below 200 K in Fig. 5). Our recent detailed analysis of the dielectric dispersion between  $T_{\text{VF}}$  and  $T_{\text{d}}$  revealed two relaxations, which were well fitted using two Cole-Cole formulas which express the flipping and breezing of polar nanoregions.<sup>82</sup> The former one disappears below  $T_{\text{VF}}$  ( $\tau_1$  diverges) and the latter one appears below  $T^*$ , where the static polar nanoclusters start to appear (depending of the material,  $T^* = 350 - 450$  K) and its  $g(\tau)$  anomalously broadens below the freezing temperature, as explained above.

Phonons in relaxor ferroelectrics were also frequently investigated. Inelastic neutron scattering spectra revealed a drop down of the soft optical phonon branch and its merging with an acoustic phonon branch at the critical wavevector  $q_{\text{wf}}$  and its disappearance below  $q_{\text{wf}}$  at temperatures between  $T_{\text{VF}}$  and  $T_{\text{d}}$ .<sup>83</sup> This effect was called a phonon waterfall and it was at first explained by a phonon scattering on the polar nanocluster boundaries.<sup>84,85</sup> Our later inelastic neutron scattering studies found that the critical wave vector  $q_{\text{wf}}$ , below which the phonon waterfall appears, depends on the choice of the Brillouin zone and therefore the relation of  $q_{\text{wf}}$  to the size of the polar nanoregions is highly improbable.<sup>86</sup> We explained the phonon waterfall phenomena by a coupling of the acoustic and optical phonon branches. Observation of



**Fig. 5.** Frequency dependence of real and imaginary parts of dielectric function in  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  taken at various temperatures. Modified from ref. 80.

different  $q_{\text{wf}}$  in various Brillouin zones was explained by different structure factors.<sup>86</sup>

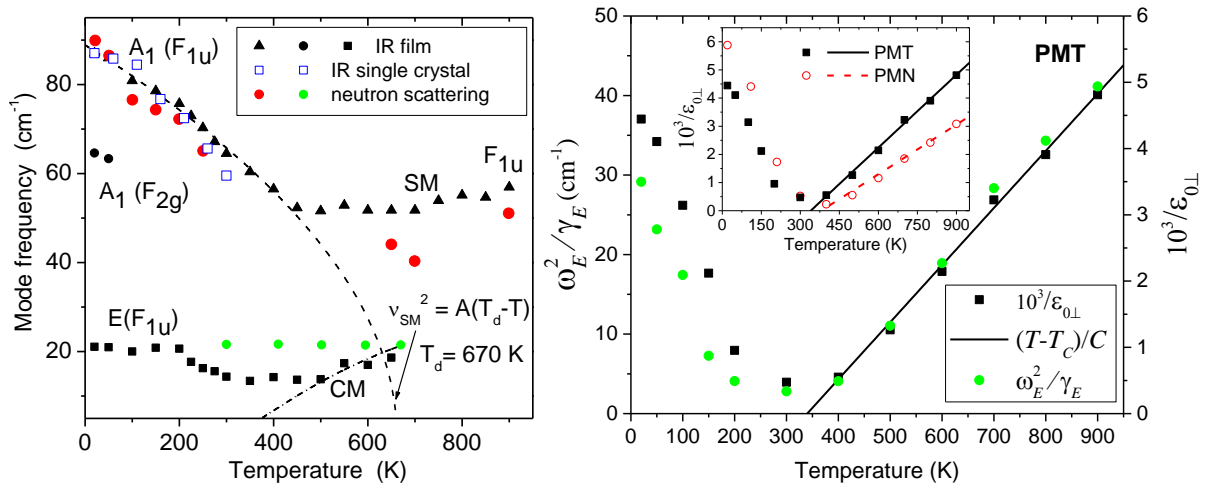
Nevertheless, below  $T_{\text{VF}}$  and above  $T_{\text{d}}$ , a soft optical phonon was observed in inelastic neutron scattering spectra of PMN with critical temperature around  $T^* = 400$  K.<sup>83</sup> The same optical soft mode was also observed in the IR spectra, but in contrast to the inelastic neutron scattering spectra, the underdamped soft phonon was observed at *all* temperatures (including temperatures between  $T_{\text{VF}}$  and  $T_{\text{d}}$ ) not only in PMN (Fig. 6),<sup>87</sup> but also in PLZT,<sup>75</sup> PMT<sup>77</sup> and  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ .<sup>88</sup> Earlier spectroscopic data<sup>87</sup> have shown that below 400 K, the soft phonon in PMN follows the Cochran law with the extrapolated critical temperature corresponding to the Burns temperature  $T_{\text{d}}$  (Fig. 6a). Nevertheless, at higher temperatures the soft mode hardens slower than the Curie-Weiss law and the Lyddanne-Sachs-Teller relation describing the experimental  $\varepsilon'(T)$  require. Moreover, an additional overdamped central mode was observed below  $T_{\text{d}}$  (Fig. 6a), whose activation was explained by a splitting of the soft mode due to a local breaking of cubic symmetry in polar clusters.<sup>87</sup> Based on inelastic neutron scattering experiments, Vakhrushev and Shappiro proposed the soft mode splitting also above  $T_{\text{d}}$  and they claimed that both components exhibit minimum near  $T_{\text{d}}$ , but their phonon parameters had high error bars due to the high phonon damping above  $T_{\text{d}}$ .

For that reason we have performed detail THz and IR studies of relaxor PMN and PMT up to 900 K and fitted the spectra to the Bruggeman effective medium formula.<sup>82,89</sup> Six polar phonons observed at 900 K gave evidence about the non-cubic local structure above  $T_{\text{d}}$ , since the cubic perovskite structure allows only three polar phonons in the IR spectra. We clearly observed the *E*-component of the soft mode polarized perpendicularly to local polarization



( $\mathbf{P}||[111]_{\text{cub}}$ ) in polar nanodomains, which is overdamped at all the temperatures, while the  $A_1$  component is underdamped at all temperatures. Both soft phonons exhibit clear shifts with temperature. The  $E$  mode component exhibits softening towards  $T^*=350$  K and 400 K in PMT and PMN, respectively, and hardening below this temperature (Fig. 6b).

Static permittivity  $\epsilon'_{0\perp}$  calculated from the  $E$  mode contributions follows the Curie-Weiss behavior above 400 K (Fig. 1b) which corresponds to previous observations above  $T_d$ .<sup>90</sup> Deviation from Curie-Weiss dependence, previously observed below  $T_d$  in the low- and radio-frequency dielectric data,<sup>90</sup> can be explained by appearance of dielectric relaxations at lower frequencies<sup>82</sup> which mask the high-frequency dielectric peak at  $T^*$  (see the EMA peak calculated using effective media approximation in Fig. 3). The  $E$  mode softening towards  $T^*$  is a hint of a local symmetry-lowering of the crystal structure within the polar nanodomains.



**Fig. 6.** Left: Temperature dependences of the polar phonon frequencies in PMN. Solid points mark data obtained on PMN thin film, open circles and squares are soft mode frequencies from inelastic neutron scattering and IR reflectivity of PMN single crystal. After Ref. 87. Right: Temperature dependence of the reciprocal static permittivity  $1/\epsilon_{0\perp}$  (solid squares) obtained from the EMA fit of  $E$ -component IR and THz spectra. Solid lines are results of the Curie-Weiss fit. Solid green circles mark the overdamped  $E$  component of the soft mode frequency characterized by  $\omega_E^2/\gamma_E$ . Inset:  $1/\epsilon_{0\perp}$  of PMT compared with that of PMN. From Ref. 89.

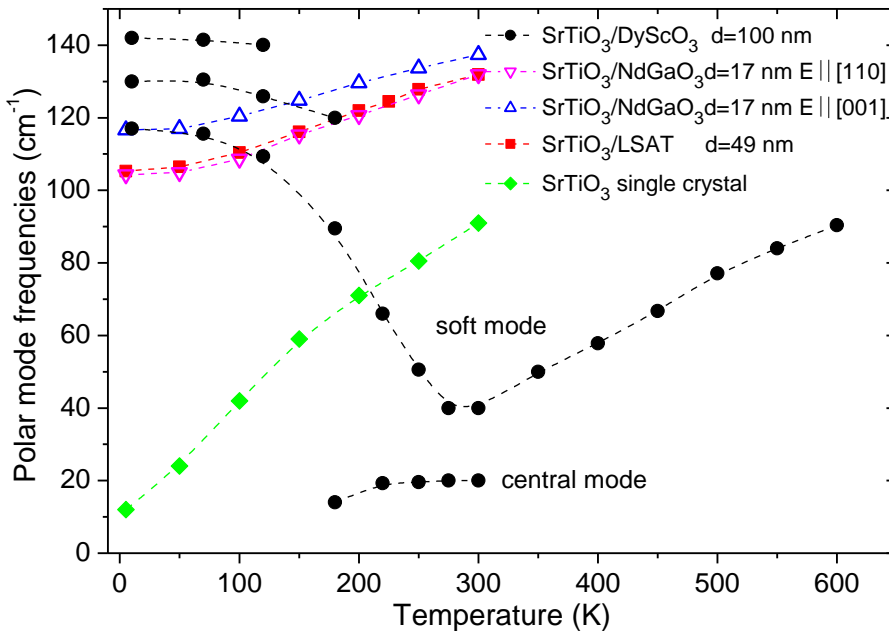
## 5. Strain-induced ferroelectric phase transitions in incipient ferroelectrics

Incipient ferroelectrics are paraelectric materials exhibiting a large increase of the permittivity on cooling due to a phonon softening as follows from the Lyddane-Sachs-Teller relations. The permittivity usually saturates at low temperatures, but the FE PT does not occur due to quantum fluctuations, hence these materials are also called quantum paraelectrics. The most famous incipient ferroelectrics are  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  and because their quantum

paraelectric phases are very sensitive on any perturbations like doping, strain or electric field, the FE phase can be easily induced in these systems.<sup>66</sup>

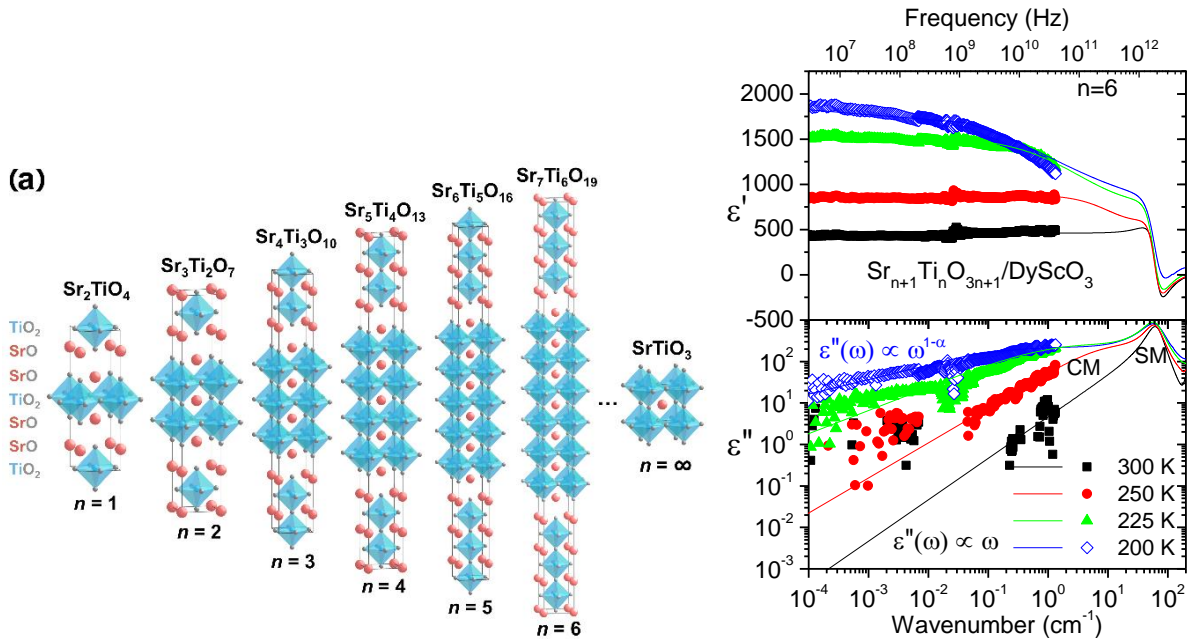
Choice of the substrate is the key factor for the strain, as the lattice mismatch leads to tensile or compressive strain in thin films. In 2004 it was proved that 1 % tensile strain caused by the DyScO<sub>3</sub> substrate can induce a FE PT near 300 K in SrTiO<sub>3</sub>.<sup>91</sup> We have shown that the PT is driven by the in-plane polarized FE soft mode, i.e. it is of the displacive type.<sup>92,93</sup> On the other hand, the ~1% compressive strain caused by NdGaO<sub>3</sub><sup>94</sup> or (LaAlO<sub>3</sub>)<sub>0.29</sub>-(SrAl<sub>1/2</sub>Ta<sub>1/2</sub>O<sub>3</sub>)<sub>0.71</sub> (LSAT)<sup>95</sup> substrates caused dramatic stiffening of the in-plane polarized soft-mode frequency (Fig. 9), so the FE PT cannot be revealed from the IR spectra. Nevertheless, the soft phonon polarized normal to the film plane (unfortunately, not active in near-normal IR reflectance geometry) should induce the FE PT in compressively strained SrTiO<sub>3</sub> grown on LSAT substrate, because the FE polarization  $\mathbf{P}||c$  was revealed in second harmonic generation studies.<sup>96</sup> Influence of various substrates, film thicknesses, grain size and their boundaries in films and ceramics of SrTiO<sub>3</sub> on phonons is reviewed in Ref. <sup>97</sup>.

SrTiO<sub>3</sub> is the  $n = \infty$  member of the Sr<sub>n+1</sub>Ti<sub>n</sub>O<sub>3n+1</sub> homologous series. Bulk Sr<sub>n+1</sub>Ti<sub>n</sub>O<sub>3n+1</sub> crystallizing in Ruddlesden-Popper structure (Fig. 10a), exhibit incipient FE behavior and their permittivity increases with the number of perovskite layers  $n$ .<sup>98,99</sup> In 1% tensile strained



**Fig. 9.** Temperature dependences of the soft mode frequencies in SrTiO<sub>3</sub> crystal and strained films grown on various substrates. Compressively strained films grown on NdGaO<sub>3</sub> or LSAT substrates exhibit stiffening of the soft mode with respect to the crystal, while tensile strained SrTiO<sub>3</sub>/DyScO<sub>3</sub> exhibits a soft mode anomaly and appearance of the central mode near 300 K due to a high lattice anharmonicity near strain-induced FE PT. Below ~180 K, two new modes activate above 120 cm<sup>-1</sup> in this film due to the antiferrodistortive PT within the ferroelectric phase. From Ref. 97.

$\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  films grown on  $\text{DyScO}_3$ , FE PTs were observed in samples with  $n \geq 3$  with  $T_c$  increasing with the rising number of perovskite layers  $n$ .<sup>100</sup> THz transmission and IR reflectivity spectra reveal the FE soft mode, which drives the FE PT, but near  $T_c$  the dielectric strength of a central mode dominates.<sup>101</sup> The  $n = 6$  film ( $\text{Sr}_7\text{Ti}_6\text{O}_{19}$ ) shows  $T_c = 180$  K, high  $E$ -field tunability of permittivity and exceptionally low dielectric loss at 300 K which overcomes all the known tunable MW dielectrics.<sup>100</sup> Detail analysis of the MW, IR and THz spectra shows that the low room-temperature MW loss in this film has the origin in absence of the central mode at 300 K (Fig. 10b), while the high tunability of permittivity is due to sensitivity of the soft mode to the  $E$ -field.<sup>101</sup> The strain quickly relaxes with increasing  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  film



**Fig. 10** a) Schematics of the crystal structure of a unit cell of the  $n=1-6$  and  $n=\infty$  members of the  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  homologous series. b) Complex dielectric spectra of a strained  $\text{Sr}_7\text{Ti}_6\text{O}_{19}$  thin film measured at different temperatures. The points are experimental data between 3 MHz and 40 GHz. The curves show results of the fits to the experimental MW and far IR spectra. At room temperature the MW loss is low, because it is determined only by the phonon contributions (Eq. 2), while at lower temperatures a dielectric relaxation (central mode) enhances the MW loss. From Ref. 101.

thickness, which limits its application. Recently, it was proved that if one  $\text{SrTiO}_3$  layer in  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  is replaced by  $\text{BaTiO}_3$ , the chemical pressure reduces the strain, thicker films can be grown and simultaneously excellent MW properties are kept.<sup>102</sup> Today's best room-temperature MW tunable dielectric parameters were achieved in films of  $\text{Sr}_6\text{BaTi}_6\text{O}_{19}$ , where unprecedented low loss at frequencies up to 125 GHz was observed.<sup>102</sup> This makes this film very attractive for high-frequency applications in 5G telecommunications.

The second most popular incipient FE is  $\text{KTaO}_3$ , where only two publications were devoted to the IR and THz SM studies,<sup>103,104</sup> but the soft mode was also studied in details using the hyper-Raman scattering.<sup>24</sup> In Ref. 104 the chemical solution deposited polycrystalline (grain size  $\sim 160$  nm) film ( $d \approx 200$  nm) on (0001) sapphire substrate, partially (001) oriented, was shown to be FE with a diffuse  $T_C \approx 60$  K. The reason for it was shown to be the compressive strain due to larger thermal expansion of the sapphire compared to  $\text{KTaO}_3$  (the film was annealed at  $900^\circ\text{C}$ ), which could induce a FE phase with preferential out-of-plane orientation of  $P_s$ . In spite of it a minimum in the frequency of the in-plane polarized soft mode was observed near  $T_C$ ,<sup>104</sup> while in crystal and ceramics the soft mode gradually softens on cooling and levels off at  $\sim 20$   $\text{cm}^{-1}$  below 20 K.<sup>24,105</sup>

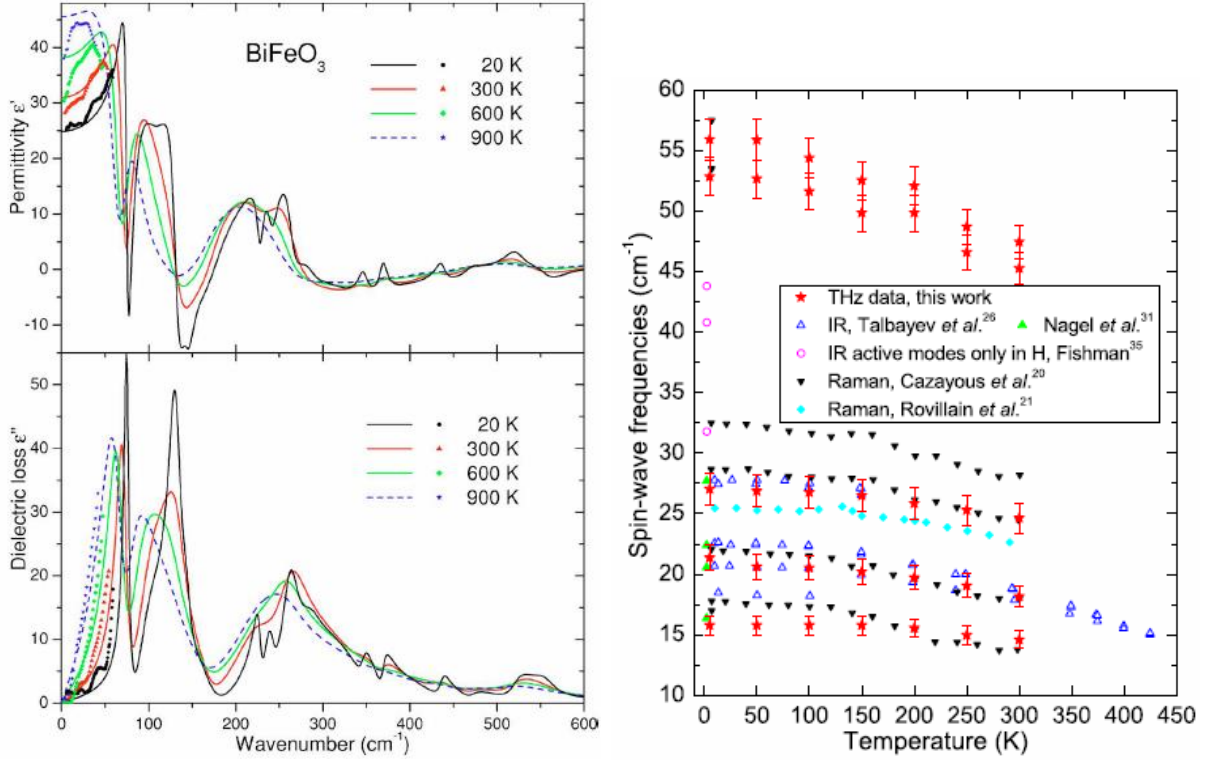
## 6. Soft-mode spectroscopy in multiferroics with displacive ferroelectric phase transitions

Multiferroics are materials exhibiting magnetic and FE order simultaneously. Since the magnetization can be controlled by the electric field (i.e. magnetoelectric effect) in these materials, they have high promising potential for applications in spintronics and nonvolatile memories and therefore they are intensively studied. In this chapter we will focus on type-I multiferroics, where FE and magnetic phases appear independently and therefore their magnetoelectric coupling is relatively small.

The most studied multiferroic is  $\text{BiFeO}_3$ , because it is one of the few single-phase room-temperature multiferroic with high FE  $T_C = 1120$  K and antiferromagnetic Néel temperature  $T_N = 643$  K. Unfortunately, its magnetoelectric coupling is weak and the 1.2 % change of its permittivity with magnetic field (magnetodielectric effect) observed above 200 K is mainly caused by a combination of magnetoresistance influencing related Maxwell-Wagner dielectric relaxation in electrically leaky samples.<sup>106</sup> In the insulating phase (i.e. below 200 K) the magnetodielectric effect drops down below 0.3 % in the magnetic field 9 T. The effect is small because the linear magnetoelectric effect is forbidden in incommensurately modulated cycloidal magnetic structure. Only above 19 T the antiferromagnetic structure becomes unmodulated and the linear magnetoelectric effect is allowed.<sup>107</sup>

IR reflectivity and THz transmission spectra revealed 13 polar phonons which exactly correspond to the rhombohedral  $R3c$  symmetry.<sup>106</sup> On heating, the phonons broaden and gradually merge in three bands allowed in the cubic perovskite  $Pm\bar{3}m$  structure expected in the paraelectric phase. We measured the spectra up to 900 K and found an optical soft mode, which is responsible for an increase of the low-frequency permittivity with rising temperature (Fig. 11

left). Phonon softening is only partial, suggesting that the phase transition into the paraelectric phase will be of the first order.<sup>106</sup> Experimental data near  $T_c$  are missing in literature, but our conclusion is consistent with the theoretical prediction<sup>108</sup> of the first-order PT into intermediate antiferrodistortive tetragonal phase  $I4/mcm$  (1100 – 1450 K) and the cubic  $Pm\bar{3}m$  phase should be energetically stable only above 1450 K, which is temperature, where the  $\text{BiFeO}_3$  decomposes.

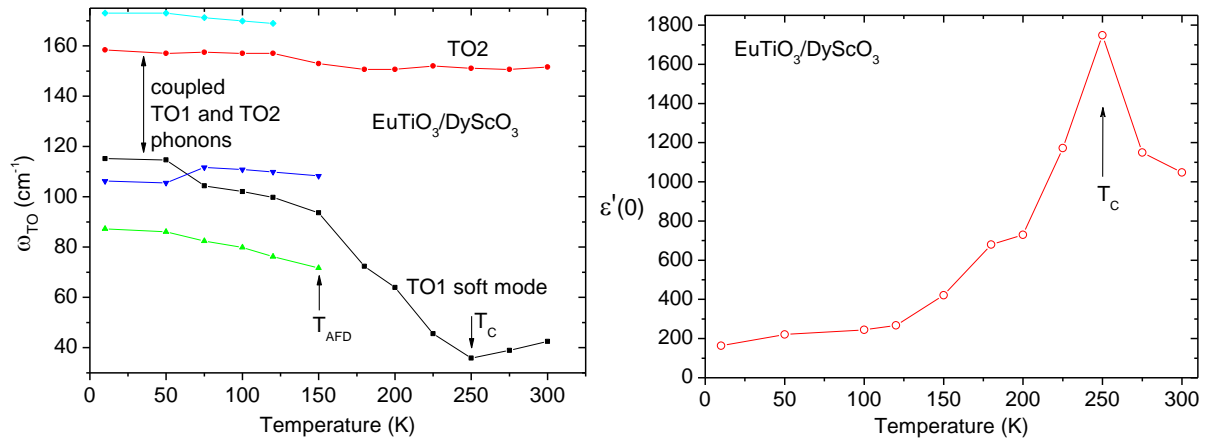


**Fig. 11** Left: Complex dielectric spectra of  $\text{BiFeO}_3$  ceramics at selected temperatures. The dots are experimental THz data; lines are results of the IR reflectivity fits. Note the shifts of  $\epsilon''$  peaks to lower frequencies due to the phonon softening on heating (from Ref. 106). Right: Temperature dependence of the electromagnon frequencies in  $\text{BiFeO}_3$  determined from the fits of our THz spectra compared with published frequencies obtained from Raman scattering and far IR spectra (from Ref. 109).

THz and Raman spectra revealed number of spin excitations, whose frequencies soften towards  $T_N$  (see Fig. 11 right).<sup>109</sup> These magnons are electrically and magnetically active,<sup>110</sup> therefore can be called electromagnons and are activated in the spectra from outside of the Brillouin zone center due to the incommensurate modulation of spins in the antiferromagnetic phase.<sup>111</sup>

Fennie and Rabe<sup>112</sup> suggested theoretically a new route for preparation of multiferroics with a strong magnetoelectric coupling. They proposed to use a biaxial strain in epitaxial thin films for inducing the FE and ferromagnetic states in materials, which are in the bulk form paraelectric and antiferromagnetic. The basic condition for such materials is the strong spin-

phonon coupling. Based on their first-principles calculations, Fennie and Rabe<sup>112</sup> proposed to use EuTiO<sub>3</sub>, because this material is in its bulk form an incipient FE and its permittivity strongly changes at the antiferromagnetic PT due to the strong spin-phonon coupling.<sup>113</sup> Temperature dependence of the permittivity in EuTiO<sub>3</sub> crystal was successfully explained by strongly anharmonic behavior of the soft mode.<sup>114,115</sup> The bulk EuTiO<sub>3</sub> ceramics undergoes an antiferrodistortive PT from the high-temperature cubic  $Pm\bar{3}m$  ( $Z=1$ ) structure to the tetragonal  $I4/mcm$  ( $Z=1$ ) phase near 280 K.<sup>116,117</sup> For that reason the soft mode splits in the tetragonal phase and both components of the soft mode soften on cooling. Lee *et al.*<sup>118</sup> grew the epitaxial EuTiO<sub>3</sub> thin films on DyScO<sub>3</sub> substrates and due to the 1% tensile strain the soft mode (seen in the IR reflectance) is much softer than in the bulk, reaching a minimum frequency at  $T_c = 250$  K (Fig. 12a). Due to the soft mode anomaly, the permittivity exhibits a maximum (Fig. 12b), typical for the displacive FE PTs. FE polarization was calculated from the first principles<sup>118</sup> and also estimated based on the value of  $T_c$ <sup>119</sup> with the resulting value 20 – 30  $\mu\text{C}/\text{cm}^2$ . The non-centrosymmetric structure of the thin film has been also proven by observation of the second harmonic generation signal below  $T_c$ . Magneto-optic Kerr effect studies revealed strain-induced ferromagnetic state below 4.3 K. All these studies confirmed theoretical predictions that the strain can induce FE and ferromagnetic order in paraelectric antiferromagnets. Nevertheless, the magnetic Curie temperature  $T_c = 4.3$  K is too low for practical applications, despite of the FE critical temperature close to room temperature which can be even enhanced by a higher strain.



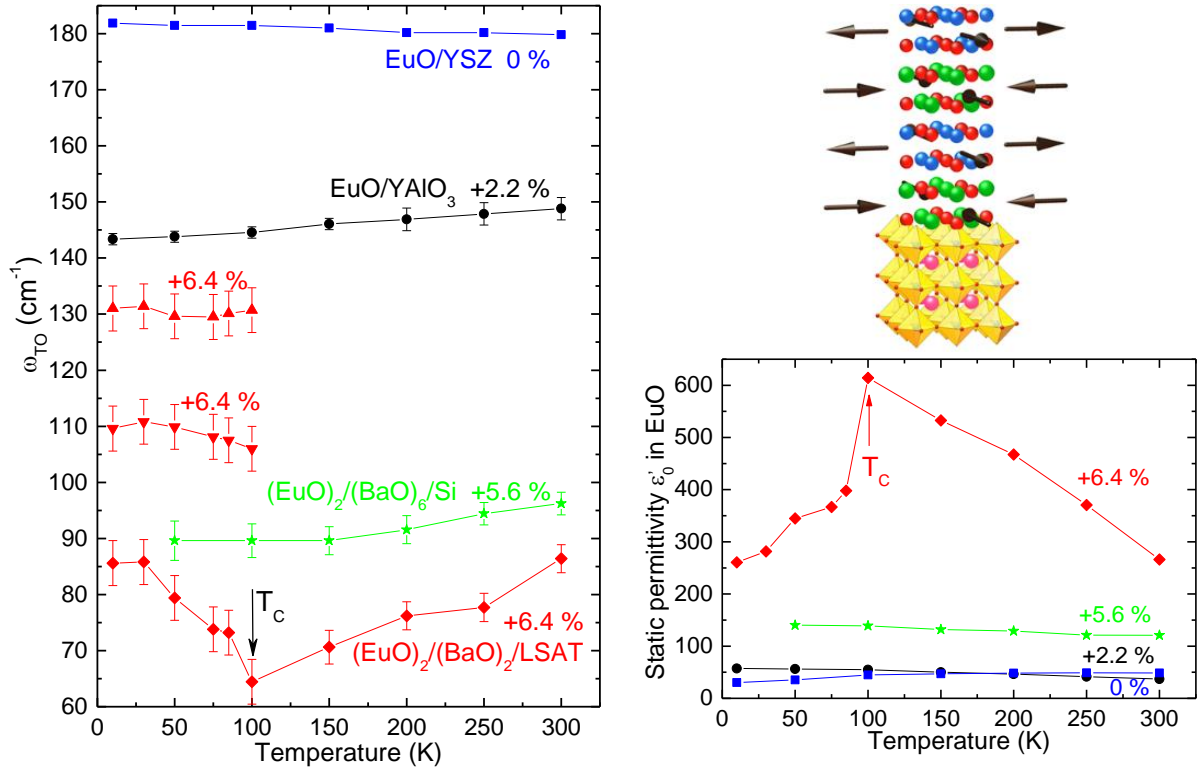
**Fig. 12** (a) Temperature dependence of the lowest-frequency phonons and (b) static phonon permittivity in the EuTiO<sub>3</sub> film grown on DyScO<sub>3</sub>. Soft mode anomaly induces dielectric anomaly at  $T_c$  and two new modes activate in the IR spectra below 150 K due to an antiferrodistortive PT at  $T_{AFD}$ . Modified after Ref. 118.

Permittivity in EuTiO<sub>3</sub> dramatically changes with the magnetic field.<sup>113</sup> Since the high value of permittivity is caused by the soft mode contribution, it is natural to expect that the soft mode

frequency will change with the magnetic field. First attempt to see the soft mode tuning in magnetic field in ceramics was not successful due to too broad reflectivity band.<sup>114</sup> Nevertheless, in compressively strained  $\text{EuTiO}_3$  films grown on LSAT substrates the soft phonon is significantly stiffened above  $100 \text{ cm}^{-1}$  and shows a rather narrow reflectance peak, whose change with magnetic field and temperature can be studied with much higher accuracy than in the bulk samples.<sup>120</sup> Actually, reliable tuning of the soft mode frequency by  $2 \text{ cm}^{-1}$  was detected in the IR reflectance spectra,<sup>120</sup> explaining in this way the magnetodielectric effect in  $\text{EuTiO}_3$ .

A FE PT can be induced also in  $(\text{Eu}_{1-x}\text{Ba}_x)\text{TiO}_3$  solid solution.<sup>121</sup>  $(\text{Eu}_{0.5}\text{Ba}_{0.5})\text{TiO}_3$  and  $(\text{Eu}_{0.5}\text{Ba}_{0.25}\text{Sr}_{0.25})\text{TiO}_3$  exhibit displacive FE PTs at 215 and 130 K, respectively, because the FE soft modes were observed in THz and IR spectra.<sup>122,123</sup> In both materials, the Néel temperature remains close below 2 K. Since  $T_N$  is very low and internal electric field is of order of 10 MV/cm in the FE phase and this field (and the FE polarization) can be switched at low temperatures by an external electric field of 3-10 kV/cm<sup>-1</sup>, the system was suggested for measurement of an electron dipole moment, which could be revealed in observation of the linear magnetoelectric effect in the paramagnetic state.<sup>121</sup> This effect is forbidden in the paraelectric state, but if the linear magnetoelectric effect would be observed, it could be explained by a non-zero electron dipole moment which violates both space-inversion and time-reversal symmetry. These are basic conditions for the linear magnetoelectric effect. A change of magnetization with electric field was really observed in  $(\text{Eu}_{0.5}\text{Ba}_{0.5})\text{TiO}_3$  at 4 K,<sup>124</sup> but since the sample heats in the field above the coercive field 10 kV/cm, the effect could be explained by a temperature change. Nevertheless, the measurement allowed to determine that the electron dipole moment should be smaller than  $6 \times 10^{-25} \text{ ecm}$  ( $e$  marks a charge of electrons).<sup>124</sup>  $(\text{Eu}_{0.5}\text{Ba}_{0.25}\text{Sr}_{0.25})\text{TiO}_3$  could be more suitable for such studies, because its coercive field is three times lower so that the sample heating could be smaller.<sup>123</sup>

Ten years ago, Bousquet et al. used density functional theory and predicted a strain-induced displacive FE PT in the ferromagnetic  $\text{EuO}$ , but since its optical phonon is highly stable, the critical strain was predicted to be around 4%. Group of D. Schlom from Cornell University began growing strained  $\text{EuO}$  thin films using molecular-beam epitaxy on various substrates to impose epitaxial strain and we investigated the phonon properties of the strained  $\text{EuO}$  films using the IR reflectance spectroscopy. We found that although the phonon frequency decreased with tensile strain as predicted, the previously predicted critical 4% tensile strain was insufficient to induce a FE phonon instability.<sup>126</sup> Hearing this news, our theory colleagues from Belgium performed new calculations using a more advanced hybrid functional and found that



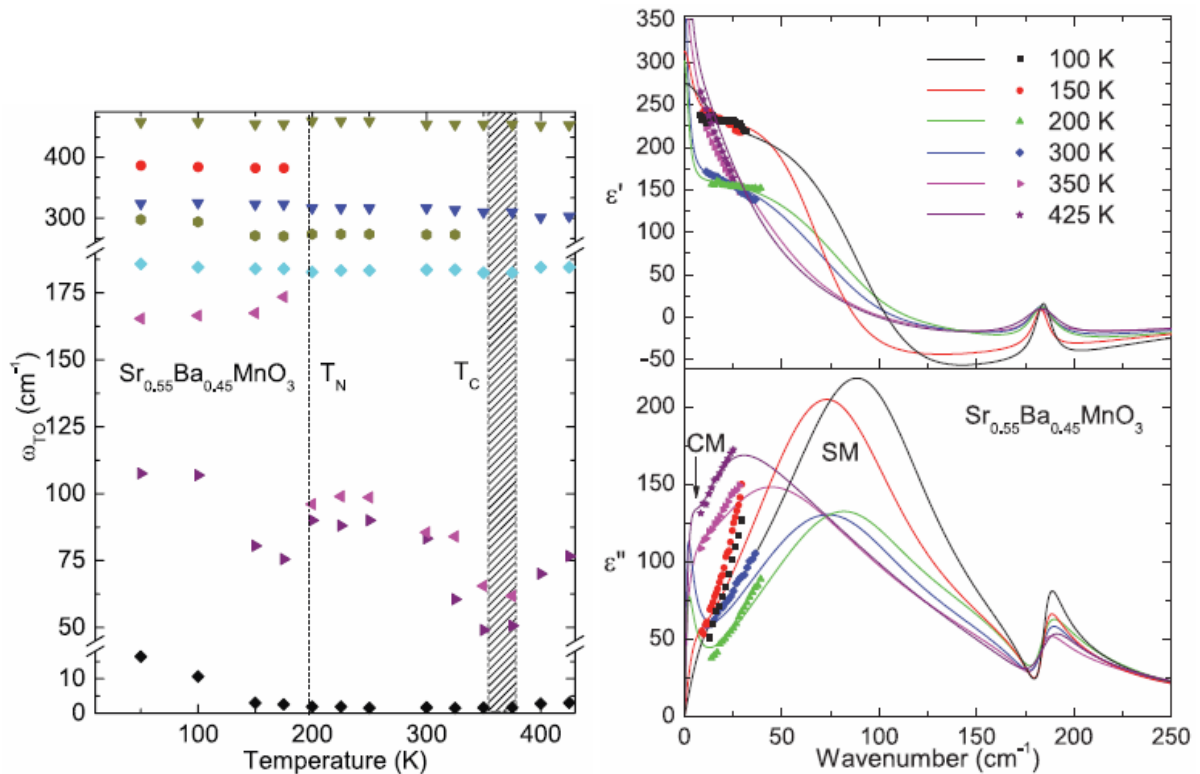
**Fig. 13.** a) Temperature dependence of the EuO optical phonon frequency in epitaxial (001)-oriented EuO films with various nominal strain levels imposed by underlying (001) YSZ, (110) YAlO<sub>3</sub>, (001) Si and (001) LSAT substrates. +5.6% and +6.4% nominal tensile strain was reached in [(EuO)<sub>2</sub>/(BaO)<sub>6</sub>]<sub>28</sub>/Si and [(EuO)<sub>2</sub>/(BaO)<sub>2</sub>]<sub>35</sub>/LSAT superlattices, respectively. The EuO phonon in the superlattice with the highest strain (+6.4%) exhibits softening typical for a displacive FE PT. Upon undergoing the PT, the single optical phonon splits into three phonons due to the reduction of the symmetry of the (EuO)<sub>2</sub> unit cell that occurs below T<sub>C</sub>. b) Schematic illustration of crystal structure of the (EuO)<sub>2</sub>/(BaO)<sub>2</sub> superlattice on an (001) LSAT perovskite substrate in which the (EuO)<sub>2</sub> layer is under biaxial tension and the (BaO)<sub>2</sub> layer is under biaxial compression. The directions of both strains are marked by arrows. Eu, Ba and O atoms are shown in blue, green and red, respectively. c) Temperature and strain dependence of the static relative permittivity of the EuO films and EuO layers in the (EuO)<sub>x</sub>/(BaO)<sub>y</sub> superlattices. The permittivity values were calculated from fits of the IR reflectance. The FE critical temperature observed for the [(EuO)<sub>2</sub>/(BaO)<sub>2</sub>]<sub>35</sub> superlattice strained to LSAT is marked by the arrow. From Ref. 126.

more than 5.8% tensile strain is required for the phonon instability and resulting FE state. Biaxially straining EuO more than 5% is challenging, as such films tend to relax after the epitaxial growth of only a few monolayers. We overcame this challenge by growing superlattices made of EuO and BaO. The latter material has a larger lattice parameter than EuO and therefore helps to maintain the tensile strain in the EuO thin layers. In (EuO)<sub>2</sub>/(BaO)<sub>2</sub> superlattices grown epitaxially on LSAT substrates we achieved 6.4% biaxial tensile strain in the EuO layers and observed a FE soft mode anomaly at 100 K, which induces a peak in the dielectric permittivity typical of a FE PT (see Fig. 13b). Magnetic measurements simultaneously proved that the superlattices remain ferromagnetic, i.e. they are multiferroic.<sup>126</sup>



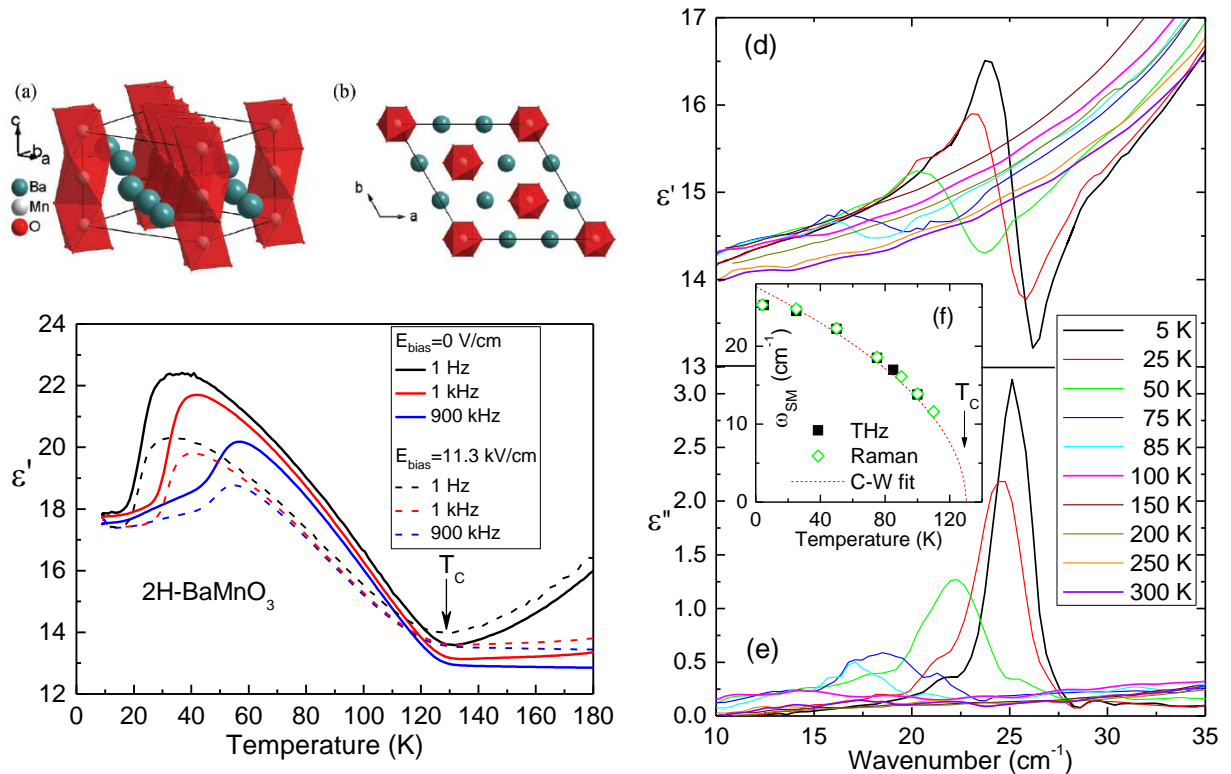
High ferromagnetic and FE critical temperatures were theoretically predicted in the strained  $\text{SrMnO}_3$  thin films.<sup>127</sup> The prediction was supported by extremely strong spin-phonon coupling in this material, which we observed near  $T_N$  in the IR spectra of  $\text{SrMnO}_3$  ceramics.<sup>128</sup> The film with 1.7% tensile strain grown on LSAT substrate exhibited FE  $T_c \approx 400$  K and Néel temperature  $T_N < 200$  K.<sup>129</sup> Nevertheless, these films were too conducting, which did not allow to study the magnetoelectric coupling. Since the FE PT should be of displacive type, we investigated the IR spectra of several strained  $\text{SrMnO}_3$  thin films, but did not obtain reliable phonon parameters, presumably due to the high phonon damping in this material. Ba substitution of Sr induces negative chemical pressure in the lattice and therefore the FE PT was observed in  $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$  crystals<sup>130</sup> and ceramics<sup>131</sup> near 350 K. The soft mode exhibits minimum at this temperature<sup>132</sup> and splits in the FE phase due to change of symmetry from cubic to tetragonal phase.<sup>131</sup> Both modes exhibit also other anomalies at  $T_N$  due to the strong spin-phonon coupling (Fig. 14).

Many type-I multiferroics exhibit improper FE PT connected with a multiplication of unit cell below  $T_c$ .  $\text{YMnO}_3$ <sup>133</sup> and also the famous  $\text{BiFeO}_3$ <sup>108</sup> belong to this family. We investigated a two-layered  $\text{BaMnO}_3$ , which at high temperatures crystallizes in nonpolar hexagonal  $P6_3/mmc$  structure and its unit cell triples below  $T_C = 130$  K and the space group changes to  $P6_3cm$ .<sup>134</sup>



**Fig. 14.** Left: Temperature dependence of the phonon frequencies in  $\text{Sr}_{0.55}\text{Ba}_{0.45}\text{MnO}_3$  ceramics obtained from the fits of IR and THz spectra. The area corresponding to  $T_c$  is hatched. Note the soft mode minimum near  $T_c$  and anomalies of the two soft mode components near  $T_N$ . Right: Complex dielectric spectra obtained from the fits of IR reflectivity and THz permittivity spectra at various temperatures. The experimental THz data are marked by dots. After Ref. 131.

Unlike in all proper ferroelectrics, where a peak in  $\epsilon'(T)$  is seen at  $T_C$ , only change of slope in  $\epsilon'(T)$  was observed at  $T_C$  (Fig. 15c), because the PT is driven by a soft Brillouin zone-boundary phonon of  $K_3$  symmetry with a wavevector  $\mathbf{q} = (1/3, 1/3, 0)$ . This IR inactive phonon is coupled with the hard zone-center  $\Gamma_2^-$  mode. Owing to the Brillouin-zone folding below  $T_C$ , the soft mode becomes a zone-center mode in the FE phase, which activates in the IR and Raman spectra and hardens on cooling. This phonon has a small dielectric strength, so it only partially explains the increase in  $\epsilon'$  below  $T_C$  (Fig. 15).<sup>134</sup> An additional dielectric relaxation, observed in the MW region, is probably due to the vibration of the FE domain walls. On cooling, this temperature-activated process slows down and the distribution of relaxation frequencies of domain wall vibration broadens. This explains the relaxor-like dielectric dispersion seen below 70 K. Contribution of domain wall motion in  $\epsilon'$  reduces under the bias electric field (Fig. 15 left) because the FE domain size increases and domain wall concentration reduces under the field. An antiferromagnetic order appears at 53 K, but short-range magnetic correlations were



**Fig. 15** Low-temperature crystallographic structure of 2H-BaMnO<sub>3</sub> featuring face-sharing MnO<sub>6</sub> octahedrons (space group  $P6_3cm$ ) from a) side view and b) top view (from Ref. 135). c) Temperature dependence of dielectric permittivity of 2H-BaMnO<sub>3</sub> ceramics measured at various frequencies and in or without bias electric field. d) Real and e) imaginary parts of complex THz dielectric permittivity showing activation and hardening of a new soft phonon below  $T_C = 130$  K. f) Temperature dependence of the soft mode frequency obtained from the THz and Raman spectra. Dashed line is the result of the fit using the Cochran law.

observed in the EPR spectra up to 230 K.<sup>134</sup>

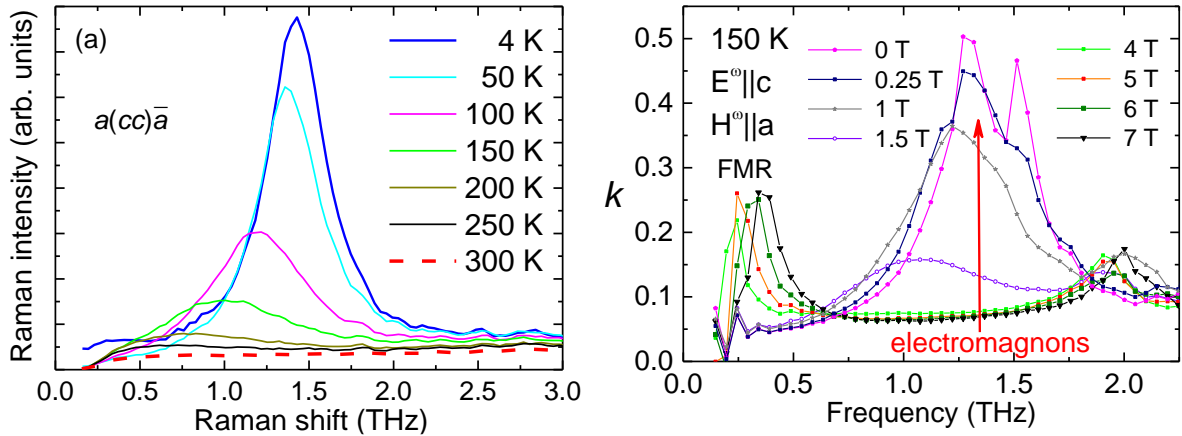
## 7. Spin-induced multiferroics

In 2003, a new class of multiferroics was discovered in TbMnO<sub>3</sub>. Kimura et al.<sup>136</sup> observed a narrow and small peak in  $\epsilon'(T)$  at the temperature, where the cycloidal magnetic structure of TbMnO<sub>3</sub> changes its modulation. Its FE polarization was 3 or 4 orders of magnitudes lower than in classical ferroelectrics, but since the polarization direction was possible to control by the direction of external magnetic field, the authors explained it as caused by the spin interactions. Due to this fact the polarization is more sensitive to magnetic field and the magnetoelectric coupling is huge. Shortly after this observation, many new spin-induced ferroelectrics were discovered, called now type-II multiferroics.<sup>137</sup> Since the order parameter of the FE PT transition is not polarization, these multiferroics belong to improper or pseudoproper ferroelectrics.<sup>138</sup> For that reason, one cannot expect FE soft phonons or critical dielectric relaxation in these materials and therefore the dielectric anomalies are small at  $T_C$ . Nevertheless, in one paper a critical relaxation in multiferroic MnWO<sub>4</sub> was reported, but it was observed in the MW region only less than 1 K above the  $T_C$ .<sup>139</sup> This soft dielectric excitation was explained by an electromagnon<sup>139</sup> coupled with the polar phonon. Just this excitation, activated in the dielectric spectra in a close proximity to the FE PT, is responsible for the tiny dielectric anomaly at  $T_C$  in MnWO<sub>4</sub> and most probably also in other spin-induced ferroelectrics.

The electromagnons (i.e. electrically active magnons) were first time discovered by Pimenov *et al.* in THz spectra of TbMnO<sub>3</sub> and DyMnO<sub>3</sub><sup>140</sup> and since that time they were observed in many multiferroics.<sup>137</sup> Characteristic feature of the electromagnon is its activity in the dielectric THz or MW spectra and its coupling with polar phonons. It means, it receives its dielectric strength from the IR active phonons. Due to off-diagonal dynamic magnetoelectric coupling, THz or MW absorption of electromagnons exhibits a directional dichroism, i.e. the absorption depends on propagation direction of the electromagnetic radiation.<sup>137</sup> We have observed electromagnons in  $\epsilon$  phase of Fe<sub>2</sub>O<sub>3</sub>,<sup>141</sup> Ni<sub>3</sub>TeO<sub>6</sub>,<sup>142</sup> Ni<sub>3-x</sub>Co<sub>x</sub>TeO<sub>6</sub>,<sup>143</sup> quadruple perovskites CaMn<sub>7</sub>O<sub>12</sub><sup>144</sup> and SrMn<sub>7</sub>O<sub>12</sub>,<sup>145</sup> Y-type hexaferrite BaSrCoZnFe<sub>11</sub>AlO<sub>22</sub><sup>146</sup> and Z-type hexaferrite (Ba<sub>x</sub>Sr<sub>1-x</sub>)<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub>.<sup>147</sup>

Interestingly, the Y-type hexaferrite exhibits an asymmetric change in static FE polarization  $P$  with magnetic field  $H$  ( $P(H) = -P(-H)$ ) whereas the Z-type hexaferrite shows a symmetric change ( $P(H)=P(-H)$ ). These facts were clarified recently: the static magnetoelectric coupling in Y-type hexaferrites can be explained only by the inverse Dzyaloshinskii-Moriya interaction

while additional  $p$ - $d$  hybridization becomes dominant in the Z-type hexaferrite.<sup>148</sup> The magnetoelectric coupling is giant<sup>149,150</sup> because the magnetic structures of hexaferrites are extremely sensitive to external magnetic field. THz and Raman spectroscopic studies of Y- and Z-type hexaferrites revealed the electromagnons in both kinds of the spectra.<sup>146,147,151,152</sup> It is plausible because all polar excitations should be both IR and Raman active in non-centrosymmetric FE phase. Our analytical calculations confirm that the electromagnons are activated by the exchange striction.<sup>146</sup> Also, we were able to determine selection rules for electromagnons in various magnetic structures of hexaferrites. Fig. 16 shows that the electromagnon in Y-type hexaferrite softens on heating towards the magnetic (and simultaneously FE) PT near room temperature so that it behaves similarly as the FE soft phonon in displacive ferroelectrics. Since the electromagnon is activated in the THz and Raman spectra only in alternating longitudinal conical magnetic structure and this structure disappears in the magnetic fields above 4 T, intensity of the electromagnon weakens and its frequency softens with magnetic field and finally this excitation disappears in the field above 4 T (Fig. 16b). On the other hand, a new excitation appears in the THz spectra below 0.4 THz in the field above 4 T. This is a ferromagnetic resonance (FMR), which linearly shifts from MW to THz region with rising magnetic field.<sup>146</sup>



**Fig. 16.** (a) Temperature dependence of the Raman scattering spectra showing the electromagnon in the Y-type hexaferrite BaSrZnCoFe<sub>11</sub>AlO<sub>22</sub>. (b) Magnetic field dependence of the extinction coefficient of the Y-type hexaferrite in the THz region measured at 150 K. In the field above 4 T, the electromagnon doublet disappears and a ferromagnetic resonance (FMR) appears in the low-frequency part of the spectra. Modified from Ref. 146.

Recent MW studies of the magnetic permeability revealed the FMR in the Z-type hexaferrite (Ba<sub>x</sub>Sr<sub>1-x</sub>)<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub> at frequencies below 2 GHz (measured without magnetic field).<sup>153</sup> Its frequency showed a linear decrease on heating towards the magnetic PT temperature 500 K, where the magnetic structure changes from conical to collinear. FMR studies performed near 9

GHz with a magnetic field up to 10 kOe also confirmed the PT near 500 K. Moreover, FMR spectra were tunable by an external  $dc$  and  $ac$  electric field which allowed to determine the value of magnetoelectric coefficient  $\alpha_E = 390$  ps/m at 170 K.<sup>153</sup> The value of  $\alpha_E$  was one order of magnitude lower than that reported at 10 K,<sup>150</sup> but still one or even four orders of magnitude higher than in other “high-temperature” multiferroics. Sensitivity of the FMR on electric field gives an evidence that the FMR has an electromagnon character.

In 2012, an unusually strong spin-order induced FE polarization was revealed in  $\text{CaMn}_7\text{O}_{12}$  below 90 K. Subsequently it was shown that the quadruple perovskites  $(\text{AMn}_3)\text{Mn}_4\text{O}_{12}$  ( $\text{A}^{2+} = \text{Cd, Sr, Pb}$ ) exhibit a similar sequence of structural PTs:<sup>154-155,156</sup> Near 400 K, they undergo

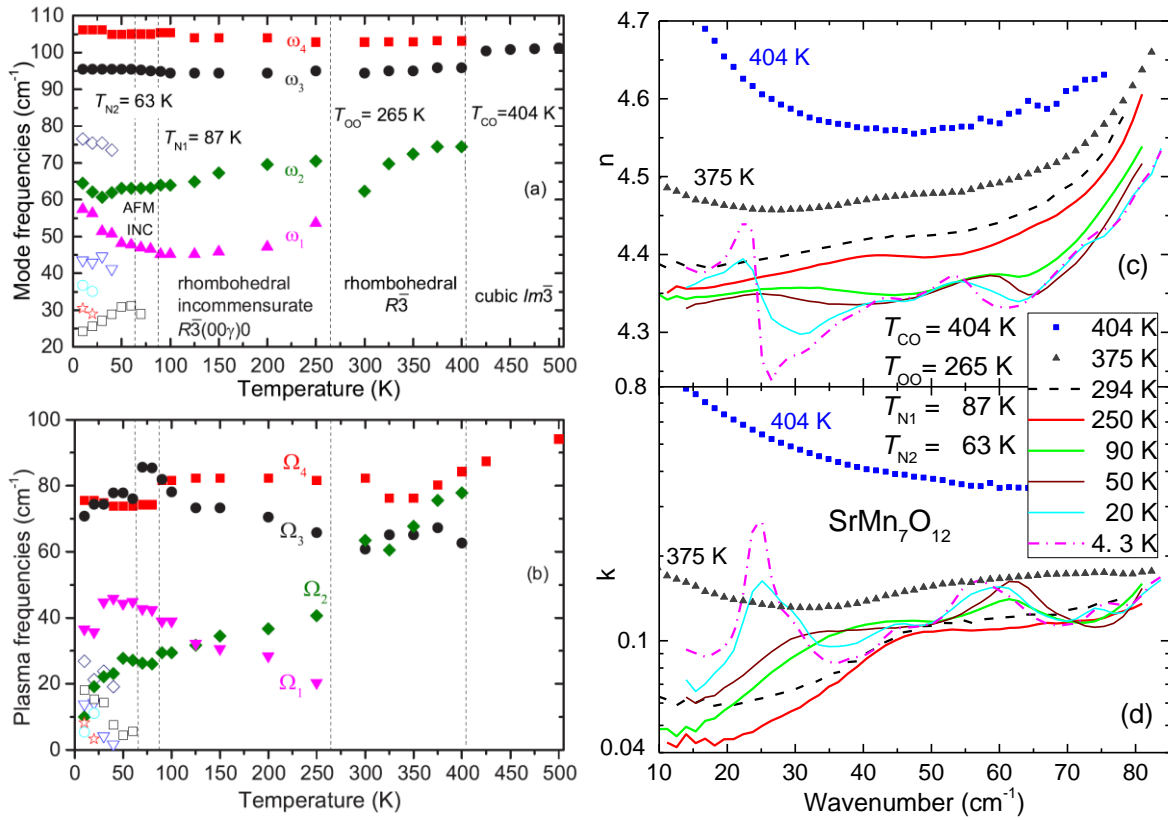


Fig. 17. Temperature dependence of (a) the low-frequency excitations and (b) their plasma frequencies  $\Omega_j = \sqrt{\Delta\epsilon_j}\omega_j$  observed in the THz and IR spectra of  $\text{SrMn}_7\text{O}_{12}$ . The open symbols correspond to spin excitations or phonons activated by breaking of the inversion center, whereas the remaining phonons are marked by solid symbols. (c) Real and (d) imaginary parts of the complex refractive index of  $\text{SrMn}_7\text{O}_{12}$  ceramics obtained from the THz time-domain spectroscopy. From Ref. 145.

a charge-ordering metal-insulator PT from a cubic to a rhombohedral  $R\bar{3}$  structure. The next PT gives rise to the Mn orbital ordering and an incommensurate structural modulation along the  $c$  axis below ca. 250 K. On further cooling, the samples show two magnetic PTs near 90 K and 40 K with PT temperatures depending on the chemical composition. The antiferromagnetic

phases are helical and incommensurately modulated. We investigated IR, THz and Raman response of  $\text{AMn}_7\text{O}_{12}$  ( $A=\text{Ca, Sr}$ ) ceramics and found similar dramatic changes in phonon spectra reflecting changes in phonon selection rules in various crystal structures (Fig 17) including new phonons appearing in the spin-order-induced FE phases.<sup>144,145</sup> The strongest variations occur in THz spectra near the two magnetic PTs (see Fig. 17c,d). They activate new modes in the spectra, with resonance frequencies and intensities changing with temperature and magnetic field. Below the lowest-temperature magnetic PT, we observed a transfer of plasma frequencies  $\Omega_1$  and  $\Omega_2$  (defined as a square roots of oscillator strength) from the low-frequency phonons to these excitations, therefore we assigned them to electromagnons, because they must be polar.

## 8. Resume

In this review, a basic concept of the FE soft modes driving the FE PTs is explained and demonstrated in materials which I investigated within the last 25 years. In Rochelle salt – the first know FE crystal – we show that although this material was for long time considered as a typical example of the system with an order-disorder PT, two coupled polar phonons show anomalous softening with rising temperature and these phonons are coupled with the MW dielectric relaxation so that this system belongs to crossover between order-disorder and displacive type of the PT.<sup>30</sup> On the other hand, another related tartate - lithium thallium tartrate monohydrate – shows a typical behavior of the displacive ferroelectrics.<sup>52</sup> Lead-based relaxor ferroelectrics with perovskite structure show a strong and soft dielectric relaxation whose distribution of relaxation frequencies anomalously broadens on cooling towards the freezing temperatures and covers the frequencies from sub-Hz up to THz region even below the freezing temperatures.<sup>75,79</sup> Although the relaxors are cubic in the whole temperature interval, the phonons are split at all temperatures due to locally broken center of symmetry in polar nanodomains and the lowest frequency phonon undergoes a critical softening towards  $T^* = 350 - 400$  K, giving evidence about a local PT in polar nanodomains.<sup>82,89</sup> In incipient FE  $\text{SrTiO}_3$ ,  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  and  $\text{KTaO}_3$ , frequencies of the soft phonons strongly reduce on cooling and saturate near liquid helium temperatures due to quantum fluctuations, but we have shown that the epitaxial strain can induce displacive FE PTs, which can be revealed in the phonon behavior.<sup>92,94,100,101,104</sup> In antiferromagnetic and incipient ferroelectric  $\text{EuTiO}_3$ , 1% tensile strain induces not only a displacive FE PT at 250 K, but the antiferromagnetic structure changes also to ferromagnetic one due a strong spin-phonon coupling.<sup>118</sup> In ferromagnetic  $\text{EuO}$ , a huge tensile strain (more than 6%) was able to induce a displacive FE PT,<sup>126</sup> even if the phonon is

highly temperature stable in the bulk EuO. Incomplete phonon softening was observed in the multiferroic BiFeO<sub>3</sub> connected with the first-order and improper FE PT at 1100 K.<sup>106</sup> Displacive character of the FE PT was revealed in the multiferroic Sr<sub>0.55</sub>Ba<sub>0.45</sub>MnO<sub>3</sub>.<sup>131</sup> The soft mode exhibits also a strong anomaly at the antiferromagnetic PT due to a large spin-phonon coupling in this material.<sup>131</sup> In multiferroic hexagonal BaMnO<sub>3</sub>, the FE soft mode was observed in the THz and Raman spectra but only below  $T_c=130$  K, because the improper FE PT related with a tripling of the unit cell occurs below  $T_c$  so that the soft mode has a wave vector from the Brillouin zone boundary in the paraelectric phase and therefore cannot be IR/Raman active above  $T_c$ .<sup>134</sup> Electromagnons were detected in the THz and Raman spectra of the multiferroic BiFeO<sub>3</sub>,<sup>109,110</sup> but also in spin-induced multiferroics with the Y- and Z-hexaferrite crystal structures,<sup>146,147</sup> as well as in quadruple perovskite SrMn<sub>7</sub>O<sub>12</sub>.<sup>145</sup> Their frequencies soften on heating towards the temperatures of the magnetic PTs similarly to the soft phonons in ferroelectrics. In hexaferrites, the magnetic structures are highly sensitive to magnetic field, therefore the electromagnons disappear from the spectra at higher magnetic fields.<sup>146,147</sup>

All these results demonstrate high ability and sensitivity of IR and THz spectroscopy for determining the type of FE PTs in various materials not only in the bulk form, but also in the ultrathin films, which can be highly strained and exhibit a behavior completely different from the bulk samples.

## 9. References

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## Selected most important publications and my contribution in these papers.

The thesis is based on the following articles. They are listed in a chronological order, which are referred to in the thesis.

1. S. Kamba, G. Schaack, and J. Petzelt. Vibrational spectroscopy and soft-mode behavior in Rochelle Salt. *Phys. Rev. B* **51**, 14998-15007 (1995). [cited 29x](#)  
*This work was created during my Humboldt scholarship at the University of Würzburg. I performed all IR and Raman spectroscopic measurements, evaluated the data and wrote the first version of the manuscript.*
2. S. Kamba, G. Schaack, J. Petzelt, and B. Brezina. High-pressure dielectric and lattice vibration studies of the phase transition in lithium thallium tartrate monohydrate (LTT). *J Phys-Condens Mat* **8**, 4631-4642 (1996). [cited 7x](#)  
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7. S. Kamba, P. Samoukhina, F. Kadlec, J. Pokorny, J. Petzelt, I. Reaney, and P. Wise. Composition dependence of the lattice vibrations in  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$  Ruddlesden-Popper homologous series. *J Eur Ceram Soc* **23**, 2639-2645 (2003). [cited 34x](#)  
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8. C.-H. Lee, N. D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J. A. Mundy, L. F. Kourkoutis, Y. Nie, M. D. Biegalski, J. Zhang, M. Bernhagen, N. A. Benedek, Y. Kim, J. D. Brock, R. Uecker, X. X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D. A. Muller, I. Takeuchi, J. C. Booth, C. J. Fennie, D. G. Schlom: Exploiting dimensionality and defect mitigation to create tunable microwave dielectrics, *Nature* **502**, 532-536 (2013). [cited 141x](#)

- American co-workers theoretically predicted strain-induced ferroelectric phase transition in  $Sr_{n+1}Ti_nO_{3n+1}$ , they grew thin films and measured microwave properties and second harmonic generation. I proposed the IR reflectance experiment (measured by V. Goian and D. Nuzhnyy from my group) which allowed me to explain the origin of observed low dielectric losses and the high tunability of dielectric permittivity. I also participated in writing of the manuscript.*
9. V. Goian, S. Kamba, N. Orloff, T. Birol, C. H. Lee, D. Nuzhnyy, J. C. Booth, M. Bernhagen, R. Uecker, D. G. Schlom, Influence of the central mode and soft phonon on the microwave dielectric loss near the strain-induced ferroelectric phase transitions in  $Sr_{n+1}Ti_nO_{3n+1}$  *Phys. Rev. B* **90**, 174105 (2014). [cited 7x](#)  
*I proposed the IR experiment, interpreted the IR spectra and wrote the first version of the manuscript. The IR measurements were performed by my PhD student V. Goian, samples were provided by American collaborators.*
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*American co-workers theoretically predicted the strain-induced ferroelectric and ferromagnetic phase transition in  $EuTiO_3$  thin films, they grew the thin films and measured second harmonic generation, structural and magnetic properties. I proposed the IR reflectance experiment (measured by my student V. Goian) for confirmation of the soft-mode driven ferroelectric phase transition, interpreted the data and wrote part of the manuscript.*
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*I organized and led the research in Prague, interpreted experimental data and wrote the first version of the manuscript. Foreign co-authors provided us the samples.*
19. S. Kamba, D. Nuzhnyy, M. Savinov, P. Toledano, V. Laguta, P. Brazda, L. Palatinus, F. Kadlec, F. Borodavka, C. Kadlec, P. Bednyakov, V. Bovtun, M. Kempa, D. Kriegner, J. Drahokoupil, J. Kroupa, J. Prokleška, K. Chapagain, B. Dabrowski, and V. Goian. Unusual ferroelectric and magnetic phases in multiferroic 2H-BaMnO<sub>3</sub> ceramics. *Phys. Rev. B* **95**, 174103 (2017). [cited 5x](#)  
*I organized and led the research in Prague, interpreted experimental data and wrote the first version of the manuscript. Foreign co-authors provided us the samples, P. Toledano wrote the part with the Landau theory.*
20. S. Kamba, V. Goian, F. Kadlec, D. Nuzhnyy, C. Kadlec, J. Vít, F. Borodavka, I. S. Glazkova, and A. A. Belik. Changes in spin and lattice dynamics induced by magnetic and structural phase transitions in multiferroic  $\text{SrMn}_7\text{O}_{12}$ . *Phys. Rev. B* **99**, 184108 (2019). [cited 2x](#)  
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*I organized and led the research in Prague, interpreted experimental data and participated in writing of the manuscript. My student J. Vít made most of the experiments, wrote the first version of the manuscript and developed the theory of IR activities of electromagnons in various magnetic structures. Foreign co-authors provided us the samples.*