ACOUSTIC-EMISSION-ASSISTED STUDY OF CRITICAL
PHENOMENA RESPONSIBLE FOR GIANT
PIEZOELECTRICITY IN RELAXOR FERROELECTRIC
CRYSTALS

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Introduction

Relaxor ferroelectrics (RFE), or relaxors, are a class of compositionally disordered ferroelectric crystals possessing peculiar structure and extraordinary electromechanical and dielectric properties, such as broad and temperature dependent relaxation distribution functions resulting in diffuse frequency dependent dielectric constants [1,2]. They exhibit extremely high piezoelectric coefficients, very large electromechanical couple factors and exceptionally high strain levels. The piezoelectric strain may reach 1.7% [3] thus outperforming even the widely used Pb(Zr1-xTi x)O3 [PZT] ceramics. The latter effect is sometimes referred to as the giant piezoelectric effect [4]. Such excellent properties make relaxors the materials of choice for new generations of electromechanical transducers in a broad range of advanced applications. The efficient direct conversion of electrical energy to mechanical work, or the giant piezoelectric (electromechanical) response, is utilized in a variety of ultrasonic and medical applications as well as in telecommunications [5].

RFEs exist in a number of crystal structures, including tungsten bronzes, such as M1−xBaxNb2O6 (M = Sr, Pb) and prototype disordered perovskites, (A'A")BO3 (A" = Pb1−3x/2La x or K1−xLi x and B = Zr yTi1−y or Ta) or A(B'B")O3 (A = Pb and B" = Zn1/2Nb1/2 or Zr1−xTi1−x). A specific example of a compound crystallizing in the tetragonal (rather than orthorhombic) tungsten bronze structure is Sr1−xBaxNb2O6 (SBN) belonging to the P4bm space group symmetry over the composition range of x = 0.2 to x = 0.8; according to the phase diagram [6] the SrNb2O6 and BaNb2O6 end members crystallize in
different structures. The framework of this structure is formed by the NbO$_6$ octahedra sharing corners to build cavities around the 12-fold A1, 15-fold A2 and 9-fold C sites. It was found for the most common SBN relaxor composition, namely Sr$_{0.75}$Ba$_{0.25}$Nb$_2$O$_6$ [7] that structure is unfilled, namely the A1 and A2 sites are occupied slightly over 80%, while Ba and Sr atoms share the A2 site in roughly 1:3 ratio and only Sr atoms are found in the A1 site; the smaller C site is empty unless hosting lower ionic radii impurities, e.g. Li, Be or Mg. The structure of perovskite-type RFEs is described in more detail elsewhere [8].

In PREs, the frequency dispersion of the dielectric constant is due to polarization fluctuations associated with the existence of polar nanometer scale regions, PNRs, forming at the so-called Burns temperature, $T_d$ [9]. Upon cooling below $T_d$ [1], the crystal structure transforms into an ergodic relaxor state where PNRs with randomly distributed directions of dipole moments exist and start growing until they reach a critical value [10] and at a temperature $T^*$ transform under local strain fields into polar nano-domains, PNDs, with permanent polarization fluctuations [11]. Further cooling enormously slows down the dynamics of PNRs and at a low enough temperature, $T_f$ (typically hundreds of degrees below the $T_d$), the PNRs become frozen into a nonergodic state, while the average symmetry of the crystal still remains cubic. The process of freezing of the dipole dynamics is associated with a large broad peak in the temperature dependence of the dielectric constant, $\varepsilon$. This peak is highly diffuse and its temperature $T_m (> T_f)$ shifts with frequency due to the dielectric dispersion. The onset of a local polarization and the various characteristic temperatures can be determined by measuring the index of refraction [9], electrostrictive strain [3], inverse dielectric permittivity [2], X-ray diffraction and neutron scattering techniques [12] and also acoustic emission (AE) [13].

Table 1 summarizes the characteristic temperatures of a great variety of RFEs belonging to the both perovskite as well as tetragonal tungsten bronze structures obtained by means of the AE measurements.

The nonergodic relaxor state existing below $T_f$ can be irreversibly transformed into a FE state by a strong enough external electric field. This is an important characteristic of relaxors which distinguishes them from typical dipole glasses. This also indicates the existence of some kind of criticality. Indeed, it has been shown [14] in the case of the best known Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$ (PMN-PT) RFE that in the electric
field-temperature-composition phase diagram a first-order paraelectric-ferroelectric phase transition terminates in a line of critical points where the piezoelectric coefficient is maximum. Near the critical point, the critical electric field \((E_c)\) needed to induce the ferroelectric polarization rotations is rather small. We have found recently [15] that in PMN-PT the \(T_m\) values are field-dependent; \(T_m\) goes through a minimum at the \(E_c\), while a concurrent maximum is observed in the corresponding AE activity. The reasons for such behavior are still unclear. In the present work, we study the critical behavior of AE in additional RFE compounds in an attempt to elucidate the mechanisms underlying the maximal release of the elastic strain energy around the critical point in the field-temperature-composition phase diagrams of these materials.

Table 1

<table>
<thead>
<tr>
<th>Compound (single crystal)</th>
<th>(T_m, \text{K})</th>
<th>(T^*, \text{K})</th>
<th>(T_d, \text{K})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(Mg_{1/3}Nb_{2/3})O_3</td>
<td>420</td>
<td>529</td>
<td>620</td>
<td>[13]</td>
</tr>
<tr>
<td>Pb(Mg_{1/3}Nb_{2/3})O_3–0.25PbTiO_3</td>
<td></td>
<td></td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>Pb(Mg_{1/3}Nb_{2/3})O_3–0.33PbTiO_3</td>
<td></td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td>Pb(Mg_{1/3}Nb_{2/3})O_3–0.4PbTiO_3</td>
<td>490</td>
<td>590</td>
<td>606</td>
<td>[13]</td>
</tr>
<tr>
<td>PbZn_{1/3}Nb_{2/3}O_3</td>
<td>403</td>
<td>505</td>
<td>730</td>
<td>[16]</td>
</tr>
<tr>
<td>PbZn_{1/3}Nb_{2/3}O_3–0.09PbTiO_3</td>
<td>450</td>
<td>510</td>
<td>730</td>
<td>[16]</td>
</tr>
<tr>
<td>PbZn_{1/3}Nb_{2/3}O_3–0.045PbTiO_3</td>
<td>435</td>
<td>502</td>
<td>730</td>
<td>[17]</td>
</tr>
<tr>
<td>PbZn_{1/3}Nb_{2/3}O_3–0.060PbTiO_3</td>
<td>445</td>
<td>504</td>
<td>730</td>
<td>[17]</td>
</tr>
<tr>
<td>PbZn_{1/3}Nb_{2/3}O_3–0.070PbTiO_3</td>
<td>452</td>
<td>499</td>
<td>730</td>
<td>[17]</td>
</tr>
<tr>
<td>PbZn_{1/3}Nb_{2/3}O_3–0.12PbTiO_3</td>
<td>465</td>
<td>508</td>
<td>730</td>
<td>[17]</td>
</tr>
<tr>
<td>PbFe_{2/3}W_{1/3}O_3</td>
<td>180</td>
<td>525</td>
<td>635</td>
<td>[18]</td>
</tr>
<tr>
<td>PbFe_{2/3}W_{1/3}O_3–0.25PbTiO_3</td>
<td>292</td>
<td>518</td>
<td>650</td>
<td>[18]</td>
</tr>
<tr>
<td>PbFe_{2/3}W_{1/3}O_3–0.37PbTiO_3</td>
<td>350</td>
<td>512</td>
<td>655</td>
<td>[18]</td>
</tr>
<tr>
<td>BaTiO_3</td>
<td>400</td>
<td>506</td>
<td>550</td>
<td>[19]</td>
</tr>
<tr>
<td>PbSc_{0.5}Ta_{0.5}O_3</td>
<td>261</td>
<td>450</td>
<td>623</td>
<td>[20]</td>
</tr>
<tr>
<td>Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3</td>
<td></td>
<td></td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>Sr_{0.75}Ba_{0.25}Nb_{2}O_6</td>
<td>332</td>
<td>456</td>
<td>623</td>
<td>[21]</td>
</tr>
<tr>
<td>KTa_{68}Nb_{32}O_3</td>
<td>259</td>
<td>310</td>
<td>620</td>
<td>[22]</td>
</tr>
</tbody>
</table>

Characteristic temperatures of relaxor ferroelectrics:
\(T_m\) – peak of the temperature dependence of dielectric permittivity,
\(T^*\) - “intermediate” temperature, \(T_d\) – Burns temperature
Experimental

The data presented in Table 1 demonstrate that the AE method has become a useful supplementary nondestructive tool for studying phase transitions and other phenomena in RFEs. Due to an external force of mechanical, thermal or electromagnetic nature, the studied material produces elastic (ultrasonic) waves, which are converted to electrical signals by direct coupling to a piezoelectric sensor. Then output of the piezoelectric sensor is amplified through a frequency-selective low-noise preamplifier, filtered and additionally amplified through an amplitude discriminating amplifier and converted to voltage pulses through an amplifier-multivibrator, which are counted and displayed in time units. Usually, the count rate, or AE activity \( \frac{dN}{dt} = \dot{N}, \ s^{-1} \) is monitored. In the following, we describe briefly the setups for AE measurements presented in Fig. 1. It is shown that the sample is placed onto the polished upper surface of a quartz glass waveguide erected into a furnace from below. A piezoelectric AE sensor (usually the PZT-19 ceramic) is pasted onto the opposite cold end of the waveguide. A polarizing microscope is placed above the furnace to monitor the domain structure of the sample. Two thermo-couples provide precise measurement of the sample temperature as well as its gradient. The AE sensor is connected to a selective low-noise preamplifier of about 40 db and 500 kHz frequency band. The latter is connected to a wideband variable amplifier up to 40 db and then to a detector and a pulse discriminator. AE signals and the thermocouples output are fed into a PC. It known that that ultrasonic acoustic events are generated in ferroelectrics during discontinuous domain wall motion, in relaxor systems during reorientation of polar regions, and during thermally or electrically stimulated transitions between different phases. Therefore, the AE was measured during heating/cooling between room temperature and 400°C at a rate of 3 K/h. Some results were compared with the temperature dependences of the dielectric permittivity and the piezoelectric constants. The AE response under electric field cycling between ±8 kV/mm was monitored at different temperatures to study the critical points of the various RFE compounds. The level of AE activity during the \( E \)-field induced phase transitions is a measure of structural distortion between the parent and target phases and of the strength of domain wall mobility.
Results and Discussion

In perovskite-structure RFEs, such as the PMN-PT-type solid solutions, the best ferro- and piezoelectric properties are found in the vicinity of the morphotropic phase boundary (MPB) separating the tetragonal (ferroelectric) and rhombohedral (relaxor) phases (in PMN-xPT, $x = 0.3 \div 0.35$) in the temperature-composition phase diagram. It is generally accepted that the T-R phase transition occurs as a rotation of polarization through monoclinic $M$- phases (one of them close to
orthorhombic, $O$ phase). The spontaneous polarization directions are: [001] for $T$, [111] for $R$ and [110] for the $O$-phase. The piezoelectric effect is due to coupling between polarization ($P$) and strain ($S$). When $P$ is along the [111]-direction, the lattice strain is small, but much larger when $P \parallel [001]$. This explains the very large piezoelectric coefficients ($d$) in RFEs as well as the large dielectric permittivity ($\varepsilon$), since these parameters are related by

$$d_{im} = \sum_{jk} 2\varepsilon_{ij} Q_{mjk} P_k,$$

(1)

where $Q_{mjk}$ are the components of the electrostrictive tensor. The associated strong AE activity around the $T_m$ (Table 1) can be also explained as due to elastic waves produced by electrically polarized elastic dipoles subjected to thermal cycling [15].

Recent numerical calculations based on the Landau theory predict unambiguously the emergence of $M$-phases under application of external electric field at elevated temperatures. This occurs at critical points (CP) terminating a line of the first order ferroelectric phase transition in the ($E$-$T$) phase diagram, and an enhancement of the $d_{31}$ piezoelectric coefficient around the CP in the PMN-$x$PT system is observed even beyond the MPB region [23].

Fig. 2. Temperature dependence of AE count rate and dielectric permittivity at 1 kHz measured in course of zero field cooling for PMN-0.33PT crystal. Black baseline at $T$-axis shows the AE background level. (From ref.[15])
In this study, we have investigated experimentally the electric field dependence of AE using a PMN-0.33PT single crystal, namely within the MPB composition. Such crystal was grown in our laboratory at the Hebrew University from the high-temperature 0.75PbO+0.25B₂O₃ flux. Several 2x2x0.5 mm³ size (001)-cut plates were detached from the flux. The composition was confirmed by concurrent measurements of the dielectric permittivity and AE temperature dependences on cooling from 440 K. The two sharp AE peaks (taken at zero field) in Fig. 2 correspond to the cubic-to-tetragonal (420 K) and tetragonal-to-rhombohedral or monoclinic (360 K) phase transitions, respectively, according to the known x-T phase diagram [24]. The 420 K peak corresponds to the \( T_m \), or \( T_{mAE} \) of the PMN-0.33PT crystal in the absence of an electric field.

Fig. 3. PMN-0.33PT crystal: (a) field dependence of \( T_m \) (measured by AE) in the FC mode; (b) field dependence of maximal AE count rate value.

Fig. 3 (a) shows the field dependence of the \( T_{mAE} \) peak values. Apparently, the dependence has a V-type shape with a minimum at a certain electric field value. Qualitatively similar results were obtained earlier for ceramic PMN-xPT samples with \( x = 0.06 \) to 0.13 [25] by determining the \( T_m(E) \) dependence from the dielectric measurements. A
striking additional result is that the intensity (count rate) of the AE has a maximum at the same field value, as shown in Fig. 3 (b). It is noteworthy that the AE activity is more intense to the right side of the maximum (higher fields). We believe that this is a result of the influence of random fields which suppress the first order phase transition at small fields and, correspondingly, do not let the AE to develop. It is tempting to relate the special behavior of AE close to the position of the minimum of $T_{mAE}(E)$ to the existence of the CP in the $E-T$ phase diagram as mentioned above. It is not clear yet if random fields alone can result in the enhancement of the AE activity under the field. It would be interesting to know if this a common feature for other RFEs.

We have further investigated the electric field dependence of the characteristic temperatures in $A(B'B'')O_3$-type ($PbSc_{0.5}Ta_{0.5}O_3$, PST) and ($A''A''')(B'B'')O_3$-type ($Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$, PBST) perovskites. PST possesses a relatively smeared dielectric maximum at $T_m \sim 280K$ and a spontaneous cubic-to-rhombohedral ferroelectric phase transformation around $T_c = 261 K$. Recent AE experiments [26] have shown an absence of AE response at $T_m$ and, instead, revealed the occurrence of a modulated incommensurate cubic-to-antiferroelectric (FE-MAFE) phase transformation, denoted as $T_n = 293 K$, i.e. taking place within the temperature regime of the relaxor ergodic state. Moreover, the application of an external dc electric field shows that $T_n(E)$ exhibits the same V-shape with a minimum at a certain field value and a $\hat{N}$ intensity maximum coinciding with the $T_m$ minimum as observed for the $T_m(E)$ and AE intensity behavior in PMN-xPT. This is shown in the upper part of Fig. 4. Such nontrivial $T_n(E)$ dependence strongly supports the suggestion that $T_n$ is related to the occurrence of AFE regions, because it is well known that in crystals with AFE long-range order the AFE-PE phase-transition temperature initially decreases with the increase in $E$ and then starts increasing [27] similarly to the data presented in Fig. 4. However, the similarity with PMN-PT requires additional mechanisms to be considered, e.g. the presence of random electric fields due to chemical $B$-site disorder in relaxors. The random electric fields have a reorientational component of the macroscopic polarization adjustable by $E$. The longitudinal random electric field component contributing to the dielectric susceptibility can described as [28]
\[ \langle \chi || \rangle = \{ |E + e|^{7/2} - |E - e|^{7/2} + \ldots \} \],

(2)

where \(e\) is the random electric field value. In fact, such mechanism was suggested for the \(T_m(E)\) dependence in PMN-xPT before [25]. According to the model, \(T_m\) has a minimum when \(E\) reaches the threshold value equaled to the random electric field, \(E_{th} = e\), and then \(T_m\) increases as happens in normal ferroelectrics with a second-order phase transition. The distribution of the random electric field longitudinal component (eq. (2)) can also explain the \(dN/dt\) behavior. Indeed, as \(E\) rises the random field longitudinal component increases quadratically as \(\text{const} + AE^2\) in weak fields, passes through a sharp maximum, and then decreases as \(E^{-1/2}\) (see Fig. 3 (b)) We assume that similar processes occur in PST near the \(T_n\). The reorienting random field electric dipoles contributing to the longitudinal susceptibility induce strain within the lattice and, consequently, induce elastic waves detected as AE. Hence, the \(dN/dt\) maximum coincides with the \(T_n\) minimum, thus reflecting the strong interaction between the external \(E\) and the internal random electric fields. The quaternary PBST compound possesses a typical canonical relaxor behavior (like pure PMN), exhibiting a widely smeared dielectric-permittivity maximum at \(T_m \sim 200K\) and no long-range ferroelectric order below \(T_m\) in the absence of E. Similarly to PST, no AE is detected around the \(T_m\), but there is a relatively weak \(dN/dt\) peak at \(T_n = 237\) K. This is shown in the lower part of Fig. 4.

![Fig. 4](image_url)

Fig. 4. Field dependencies of (a) \(T_m\) peak values (measured by FC AE) and (b) \(T_{mA}\) values for PbSc\(_{0.5}\)Ta\(_{0.5}\)O\(_3\) and Pb\(_{0.78}\)Ba\(_{0.22}\)Sc\(_{0.5}\)Ta\(_{0.5}\)O\(_3\) crystals
The quenched random fields originating from the fluctuations in local chemical order are thought to be a common feature for all RFEs. Therefore, the above phenomena observed in perovskite RFEs may be present also in the case of tungsten bronze-structure RFEs. Therefore, we have studied a representative of this structure, namely the \( \text{Sr}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6 \) (SBN-75) crystal using AE as well. Samples, 4x3 mm\(^2\) area and 1 mm thick [100]-oriented platelets, were supplied by Prof. S. Kojima of the Tsukuba University (Japan). The characteristic temperatures of SBN-75 are slightly lower than those of most of the perovskite crystals. Our AE measurements yield: \( T_d = 623 \text{ K}, \) \( T^* = 456 \text{ K} \) and \( T_m = 332 \text{ K} \) at zero field (see Table 1). When an external electric field is applied, the \( T_m \) peak values initially decrease (at low fields), reach a minimum at \( E = 0.25 \text{ kV/cm} \) and then gradually increase up to an applied field of 2 kV/cm. This is shown in Fig. 5, where the typical for perovskites V-shape of the \( T_m \) behavior (see Figs. 3 and 4) is exposed. The dependence of the AE count rates at the diffuse dielectric permittivity peak values, \( T_mAE \), also exhibits a sharp maximum at the same critical electric field value of 0.25 kV with an exponential decrease upon the field increase, in striking similarity with results obtain with the perovskite structure crystals. The explanation of these dependencies may be similar that discussed for the PST crystals in the previous paragraph.

![Fig. 5. Field dependencies of the \( T_m \) values measured by AE in the FC mode (upper curve) and of the maximal AE intensity, \( T_{mAE} \), of the SBN-75 crystal](image-url)
Finally, we address the association of the critical phenomena, especially the critical electric fields, with the AE count rate level. The general analysis of the intensity of an individual AE peak can be based on a theory of excitation of sound waves by small electrically polarized elastic dipoles subjected to thermal cycling. We have pointed out earlier [15] that the process dynamics is then described by the appropriate Landau–Khalatnikov equation, and its solution in the wave approximation is similar to that of a damped oscillator vibrating with a frequency $\omega$. Assuming that the time derivative of the vibrating elastic dipoles is proportional to the time derivative of the stress, $\sigma$, the activity (count rate) of AE can be expressed as $dN/dt = v\omega(\Delta\sigma/\Delta T)$, where $v = dT/dt$ is the velocity of heating/cooling and the stress differential can be expressed as

$$\Delta\sigma = \left[ g \left( \frac{dP^2}{dT} \right) + \frac{\varepsilon_0}{2} E^2 \left( \frac{d^2 \varepsilon_r}{dT d\eta} \right) \right] \Delta T$$

(3)

where $g$ is the electrostriction tensor, $P$ is the polarization, $T$ is the temperature, $\varepsilon_0$ is the vacuum permittivity, $E$ is the electric field and $\eta$ is the local inhomogeneous strain. The left term in Eq. (3) can be assessed only if the single crystal electrostrictive and pyroelectric properties are available. We assume anyway that the second term in Eq. (3) is dominant, and the highest AE activity is expected with the onset of sharpest changes in the $d\varepsilon_r/dT$ derivatives. This occurs through the ferroelectric-to-paraelectric phase transitions associated with the emergence of $M$-type phases (see above) at CPs in the $E$-$T$ fields. Therefore, the observed $T_m$ minima coinciding with the CPs correlate so well with the maximal AE response, and AE becomes a powerful method for the straightforward and accurate determination of the critical electric fields, $E_{CP}$, coinciding with $E_{th}$ discussed above. It is noteworthy that already in the past, in a different context, we reported [29] on a unique in situ observation of a low-field (1 kV/cm) irreversible orthorhombic-to-$M_s$ phase transition by monitoring the AE activity of PZN-0.09PT under varying [001]-oriented electric fields. The study of critical phenomena responsible for the giant piezoelectric (electromechanical) response can be thus studied also in newly emerging relaxor materials.
Conclusions

The AE method is shown to be a powerful nondestructive tool for studying most of the phase transitions the RFEs belonging to both the perovskite and tungsten bronze crystal structures. Specifically, by monitoring the AE count rate, we have been able to detect the strain relief, and thus the propagation of elastic waves, due to reorientation of random fields (polarization) associated with local fluctuations of the chemical order under an externally applied electric fields. The critical field known earlier to mark to a minimum in the peak value, $T_m$, of the diffuse dielectric permittivity temperature dependence is found to correspond to the maximum intensity of the AE at $T_m$ in all types of RFEs studied. This relatively low critical field is known to be responsible for the easy polarization switch during the first order ferroelectric transitions and thus to the giant piezoelectric and pyroelectric coefficients of the RFEs. We have shown that the value of the critical field can be easily and rapidly determined by the AE measurement.

References