Size-driven relaxation and polar states in PbMg$_{1/3}$Nb$_{2/3}$O$_3$-based system

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Nanocrystalline powders and ceramics with controlled grain size from 15 to 3000 nm of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) and (PMN)$_{0.65}$-(PbTiO$_3$)$_{0.35}$ (PMN-PT35) have been synthesized using the ball milling method. Dielectric experiments have revealed in PMN a disappearance of relaxation below $\approx$30 nm grain size and combined x-ray and Raman experiments the vanishing of correlations between polar nanoregions (PNRs). A similar study in morphotropic compound PMN-PT35 has shown the appearance of a relaxor state below $\approx$200 nm, associated to a destruction of the ferroelectric domains state towards PNRs in a paraelectric matrix. These phenomena are discussed in connection with pressure experiments from the literature and on the basis of polar states destabilization by both elastic and electric random fields changes associated with the size reduction.

I. INTRODUCTION

It is well known that weak changes in grain size, composition, electric field, local strain, etc., can completely modify the physical properties of ferroelectric compounds. These effects are of uttermost importance for industrial applications of these compounds in the form of thin films or in the form of ceramics. Even in the case of "simple" perovskite such as BaTiO$_3$ (Ref. 1) or PbTiO$_3$ (Refs. 2–4) these effects are far from being clarified and intense research efforts are still made. Moreover both theoretical and experimental results[5] have shown that these effects are extremely strong in the case of PbTiO$_3$ (PT)-based solid solutions with perovskite structures, particularly in the concentration range of the so-called morphotropic phase boundary (MPB) where ultrahigh piezoelectric properties are obtained. In this case the polarization is no more restricted to an axial symmetry but can rotate freely with temperature, concentration, electric field etc inside the mirror plane of a low symmetry phase. Correlations between these giant properties and the long and short range polar order as well as possible chemical order have been intensively and fruitfully explored, for instance, in Pb(Zr, Ti)O$_3$ (PZT),[5] Pb(Mg, Nb, Ti)O$_3$ (PMN-PT),[5,6] Pb(Zn, Nb, Ti)O$_3$ (PZN-PT),[5,6] and more recently in Pb(Sc, Nb, Ti)O$_3$ (PSN-PT).[7]

As the situation in bulk materials was scarcely known and the relevant parameters begin just to be identified, almost no observations have been reported up to now on structural evolutions in MPB nanostructured materials. In the case of such compounds the effect of size reduction but also internal strain, surface effect, compression/extension due to the substrate (in the case of films), etc., are eventually added and the situation gets even more complex. Nevertheless both practical use of nanostructured materials in daily life utilization and fundamental knowledge require obviously the possibility to study these nanostructured materials in a large range of grain sizes, from the standpoint of the physical (dielectric, piezoelectric etc) properties, as it is usually done, but also regarding their structural evolution.

Up to now the size effect in perovskite lead-based solid solutions have been essentially studied in compounds with grain size of 100 nm and above, mainly in PZT;[8] regarding PMN-PT system, since pioneering works[9,10] in PMN, there are some reports of the influence of the grain size in films with perovskites structure with high (76%) concentration of PT.[11] In the case of MPB compounds, to our knowledge no study exists.

Therefore we have performed a comparative study of PMN and PMN-PT with 35% of PT (PMN-PT35) powders and ceramics synthesized using the ball milling method with controlled grain size from 15 to 3000 nm. The aim of this study is to make a comparative study in two classes of materials: a relaxor compound (PMN) and a MPB compound (PMN-PT35), both the physic and properties of which are closely connected but in which the expected effects of reduction of size are different. Indeed whereas strong effects are expected in MPB compounds, the influence in relaxor is more questionable and should result from possible interaction of the polar nanoregions (PNRs), responsible for the intriguing dielectric properties, and the grain sizes, grain boundaries, local strains, etc.

II. EXPERIMENTAL

Mechanical activation is a well-known method of synthesis in which the solid state reaction is activated by mechanical energy rather than temperature. It has been recently shown to be an effective method for the production of fine grained perovskite structured powders such as BaTiO$_3$, PT, PZN, PZT, PMN-PT.[12,13] We have used a Retsch mill PM 400 specially equipped for mechanical alloying. Typically 4 and 64 h were necessary to obtain pure perovskite phase of PMN and PMN-PT35, respectively, from the starting oxides. In the case of PMN, in order to avoid formation of pyro-
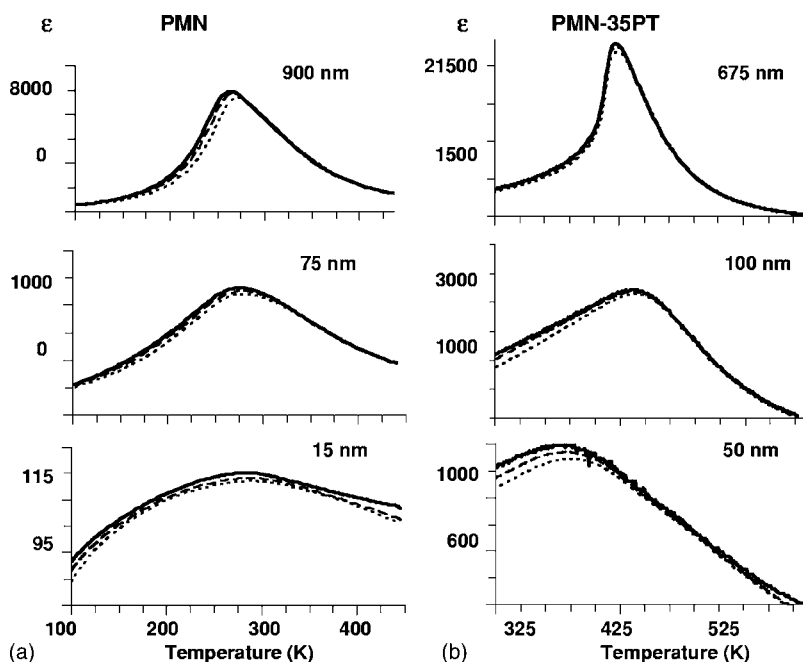
FIG. 1. Temperature and grain size dependence of dielectric constant in (a) PMN (left) and (b) PMN-PT35 (right). Plain, dotted and dashed line correspond to frequency ranges between 1 and 100 kHz.

chlore we have used an original route based on the columbite method for the synthesis of ultrafine powder of $MgNb_2O_6$, elaborated by the freeze-drying method,[14] starting from ammonium niobium oxalate (CBMM) and magnesium nitrate hexahydrate $Mg(NO_3)_2$, $6H_2O$ (99%, Strem chemicals). The solution was nozzle-sprayed into liquid nitrogen and the frozen droplets with $MgNb_2O_6$ composition were then slowly heated to 50 °C in a low-pressure chamber (3.5 Pa) to sublimate the solvents; this was followed by calcination at 850 °C for 1 h. Nanopowders with grain size in the range of 15 to 250 nm were prepared by annealing the as-prepared powders at temperatures between 450 to 950 °C for typically 30 min. In order to get ceramics the 15 nm powders were uniaxially pressed at 300 MPa. Sintering the pellets between 550 and 1200 °C for 2 h 30 min, gave ceramics with mean grain sizes between 15 up to 3000 nm and corresponding relative density between 60 and 97 %. During this process, in order to avoid PbO evaporation, the pellets were embedded in a mixture of PMN and Al_2O_3 powders. The size distribution of the powders and ceramics was measured by scanning electron microscopy and the average grain size was also checked by conventional x-ray diffraction: we obtained typical values of distribution between 10 and 20 % of the mean grain size.

High resolution x-ray diffraction measurements were performed on a highly accurate two-axis diffractometer in a Bragg-Brentano geometry with Cu-K_β wavelength issued from an 18 kW rotating anode generator, using a cryofurnace operating between 80 and 450 K. Raman spectrometry was performed at room temperature on a backscattering Fourier transform Bruker IFS66-FRA106 at $\lambda = 1064$ nm with a nitrogen cooled detector. The temperature dependence of the dielectric constant was measured at various frequencies in a temperature range from 100 to 800 K using a Hewlett-Packard 4192A impedance analyzer.

III. RESULTS

A comparative evolution with mean grain size of the dielectric constant ε thermal dependence is shown in Fig. 1 for PMN and PMN-PT35. In order to take into account the difference of porosity, the data have been corrected using the Rushman and Striven equation,[15] which gave in this case equivalent results to a simple normalization by the relative density.

For the highest grain size one observes well-known features. (1) For PMN a strong anomaly of ε in a large temperature range with high frequency relaxation, i.e., a change of the temperature of maximum with the applied frequency; this phenomenon is classically associated to the existence of correlated dynamical PNRs which freeze at low temperature, the overall matrix being paraelectric (2) for PMN-PT35 high values of ε associated to a ferroelectric phase transition, with no dielectric relaxation.

When the grain size is reduced, a continuous decrease of the maximum of the dielectric constant ε_{max} (Fig. 2) and an increase of temperature range of anomaly is observed for both compounds; however, the deviation from classical Curie law as measured by the γ coefficient deduced from fitting of the well-known Martinera and Burfoot[16] law does not change with grain size and is about 1.7–1.8 in both compounds. The effect on the T_{max} is different in both compounds (Fig. 3): in PMN a small increase (about 15°) and a huge decrease (more than 100) for PMN-PT35.

At the lowest size (r below ≈ 30 nm, not shown) no dielectric anomaly is detected in PMN-PT35 whereas a diffuse but clear anomaly is still observed for $r \approx 15$ nm in PMN [lowest part of Fig. 1(a)]. However, the two most striking results are evidenced on Fig. 4. Indeed, when the size decreases, in PMN a drastic diminishing [$\Delta T\varepsilon_{max}(f) \leqslant 1°$ for $r \leqslant r^* \approx 25$ nm] is observed indicating a disappearance of the relaxation at the lowest size, whereas on the contrary PMN-PT35 displays a transformation from a nonrelaxing ferroelectric behavior toward a relaxor state [$\Delta T\varepsilon_{max}(f) \geqslant 1°$ for $r \leqslant \approx 200$ nm]; in PMN-PT35 below 30 nm a complete vanishing of the dielectric anomaly indicates a transformation to a conventional nonferroelectric phase.
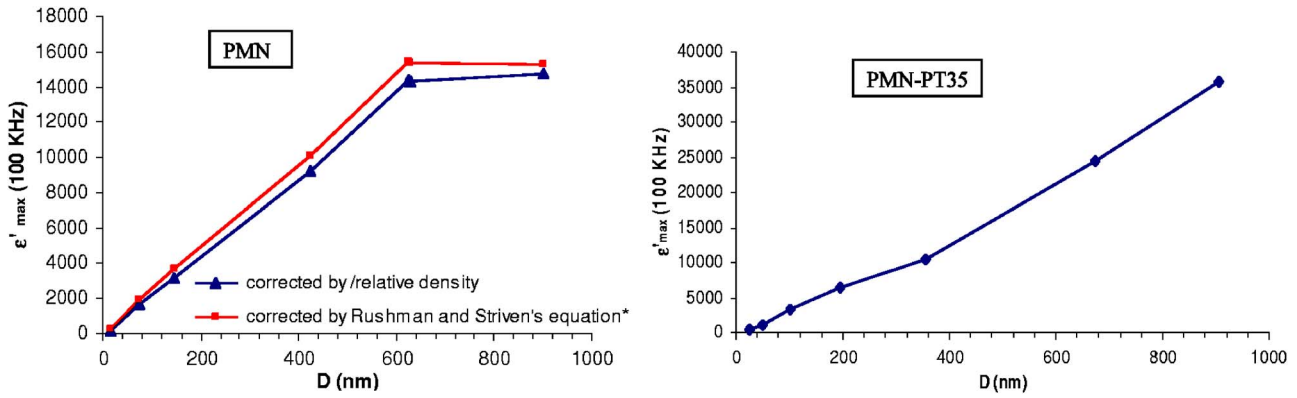
FIG. 2. (Color online) Grain size evolution of ε_{max}. The data have been corrected of the density, using the classical Rushman and Shriven equation and by normalization to the density, both corrections leading to almost the same results.

In order to get further structural information an x-ray comparative study of both compounds between the highest and the lowest size grain was performed at 300 and 80 K. In PMN-PT35 the Rietveld analysis of micrometric samples showed a mixing of monoclinic *Pm* and tetragonal *P4mm* phases, as expected from literature.[6,17] In the 15 nm powder sample of PMN-PT35 the x-ray patterns displayed large diffraction peaks as expected from a nanopowder. The Rietveld refinement of the data gave unambiguous answer to the question of the exact symmetry. Indeed it has been observed in the structural studies of MPB compounds (see, e.g., Ref. 7) that whereas many structural models can give close factor R_{wp} (which quantifies the agreement of the fitting on the profile pattern) and GoF (ratio ideally equal to 1, between R_{wp} and R_{exp}, the latter being roughly a measurement of the data statistic), a clear decrease in the R_{Bragg} (which quantifies the agreement on the integrated intensity of Bragg peaks) indicates the correct model. In the present study of PMN-PT35 with 15 nm mean grain size, a cubic phase both at 80 K (see Table I) and 300 K (not shown) is clearly evidenced by such a decrease of R_{Bragg}. This result clearly indicates that no long-range polarization exists in this compound at 15 nm grain size and that a transition from a ferroelectric state occurs below a critical size.

In PMN no change in cubic diffraction patterns was detected between the micrometric and the 15 nm samples re-

garding the Bragg peaks, except for the enlargement due to the size effect. However at 80 K strong diffuse scattering in addition to the Bragg peaks is observed in both nanosized and microsized samples (Fig. 5). In micrometric PMN this observation is well known and is connected to the existence of the PNRs, and the associated correlation length ξ have been precisely measured by Vakhrushev *et al.*:[18] below 200 K they found 20 nm. We have measured ξ in our micrometric sample at 80 K $\xi=21$ nm, in accordance with Ref. 18, whereas in the nanometric samples we found $\xi=15$ nm which is also the mean grain size of the sample.

Room-temperature Raman spectra of PMN and PMN-PT for different grain sizes are shown in Fig. 6. A detailed discussion of these spectra is out of the scope of this paper and regarding the micrometric-sized samples, has already been published by several authors; in particular we refer here to the paper by Svitelskiy *et al.*[19] and by Lima-Silva *et al.*[20] We concentrate in this study on the relevant features for the size-driven effects. Experimentally one observes a continuous decreasing of the global intensity of all modes, with slight positive or negative shifts of the associated wave numbers. At the lowest sizes a clear signal is detected in PMN whereas no more signal is evidenced in PMN-PT35 (Fig. 6).

Examination in PMN [Fig. 6(a)] of the 2 broad bands between 500 and 700 cm^{-1} (*E* band, splitted in E_1-E_2 doublet) and 700 and 900 (*B* band) is of particular interest. It has
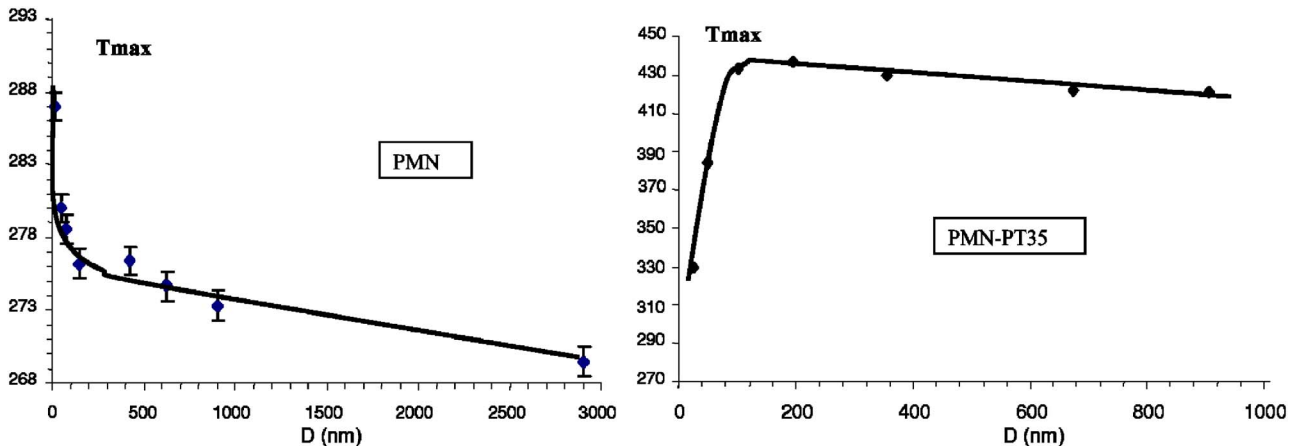

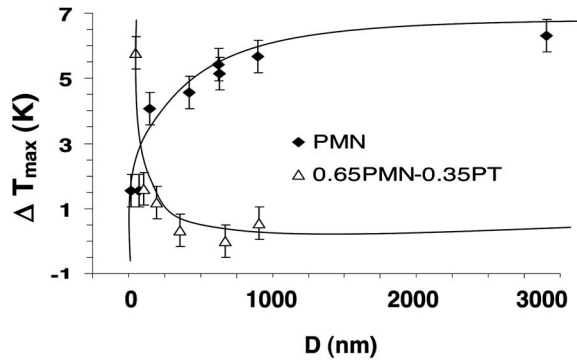FIG. 3. (Color online) Grain size evolution of T_{max}(K) at 100 kHz.

FIG. 4. Grain size dependence of dielectric relaxation, defined by $\Delta T\varepsilon_{max}(f)=T(\varepsilon_{max(f=100\ kHz)})-T(\varepsilon_{max(f=10\ kHz)})$ for PMN and PMN-PT35.

FIG. 5. (Color online) Selected part of the diffraction pattern (Cu $K_{\alpha 1-\alpha 2}$) of PMN at 80 K of a microsized and a 15 nm sample, showing the existence of the polar diffuse scattering in both patterns.

been shown[19] that the E band is associated with antisymmetric vibrations of octahedra whereas the B band can result from two contributions: one contribution associated to A_{1g} mode corresponding to chemical 1:1 ordering, the second one associated to polar vibrations of oxygen octahedra.[21–24]

Svitelskiy *et al.*[19] detected in PMN, the T^* temperature at which correlations between off-center ions become static or permanent (i.e., local phase transitions) and local distortions and strain fields appear ($T^* \approx 350$ K) in the temperature dependence of the overall band frequency [see inset of Fig. 7(a)] as well as in the critical evolution of $\Delta\nu$ of the E_1 and E_2 doublet [see inset of Fig. 7(b)], by a departure from saturation at low temperature and high temperature, respectively. We have also detected in the size dependence of these quantities [Fig. 7] a corresponding size $r^* = 30(5)$ nm, in accordance with the dielectric measurements described above. During their experiments the authors of Ref. 19 could also evidence the Burns temperature $T_d \approx 620$ K [inset of Fig. 7(a)] below which local fluctuations of polarization appear; however, we could not accede to a corresponding r_d, probably because its value is far too small.

In earlier studies,[22,25] anomaly in the relative ratio of intensity of both bands previously discussed, i.e., I_B/I_E has been related to the ferroelectric-paraelectric phase transition. Figure 8 shows such anomaly in the size dependence of

TABLE I. Rietveld agreement factors for PMN-PT35 with 15nm mean grain size at 80 K for some of the different structural models which have been tested.

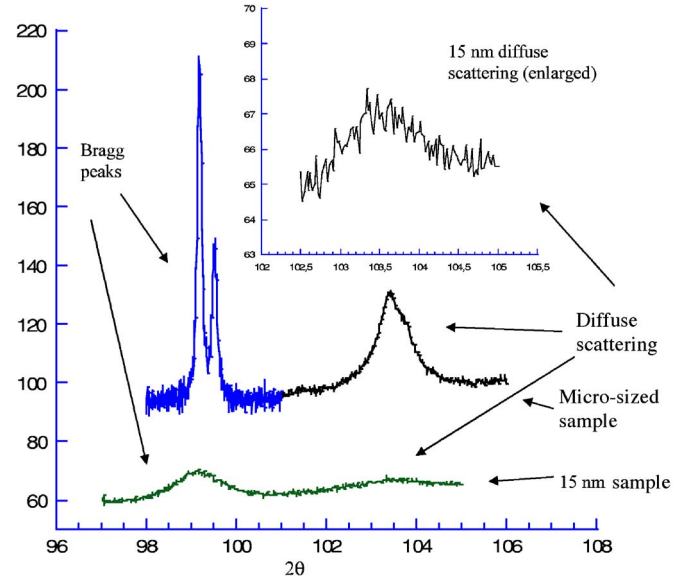| Structural model	Agreement factors		
	R_{wp}	G_{of}	R_{Bragg}
Tetragonal $P4mm$	6.65	1.22	5.51
Rhombohedral $R3m$	6.83	1.26	5.19
Orthorhombic $Bmm2$	6.63	1.22	4.36
Monoclinic Pm	6.64	1.22	5.11
Monoclinic Cm	6.88	1.26	7.78
Monoclinic+Tetragonal $Pm+P4mm$	6.75	1.24	6.70
Cubic $Pm\bar{3}m$	6.67	1.23	3.64

PMN-PT35 corresponding to the recovery of the paraelectric cubic phase when size is decreased below $r_c^* \approx 30$ nm, in agreement with our dielectric and x-ray data.

IV. DISCUSSION AND CONCLUSION

We believe that this set of experiments gives strong evidences for a new type of effects in lead-based MPB perovskites bulk material associated to the reduction in the grain size of samples. First we have observed the suppression of the relaxor effect in PMN at the lowest sizes $r \lesssim r^* \approx 30$ nm. Parallely a strong weakening of the correlations between PNRs below r^* (analog to the temperature T^*) is also evidenced by Raman scattering. The persistence of a broad anomaly in the temperature evolution of ε as well as the detection of diffuse x-ray scattering at low temperature indicate the persistence of PNRs in an overall cubic symmetry, with characteristic x-ray and Raman patterns, even in the 15-nm-size sample.

Second, in PMN-PT35 which is for the micrometric samples a nonrelaxing MPB ferroelectric compound, the appearance of a dielectric relaxation is observed for ≈ 30 nm $< r < \approx 200$ nm. Below ≈ 30 nm the vanishing of the dielectric anomaly and of the Raman signal, as well as the Rietveld analysis, indicate the recovery of a conventional (i.e., with no PNRs) cubic paraelectric phase.

When discussing physical properties of nanopowders or thin films, comparison with pressure effects is often very useful as an external hydrostatic stress applied on bulk material is considered to be similar to the internal pressure of a small particle, produced by its surface tension. In particular (hydrostatic) pressure-induced crossover from ferroelectric to relaxor state have been observed in a number of disordered ferroelectrics including PMN, La-doped PZT, and
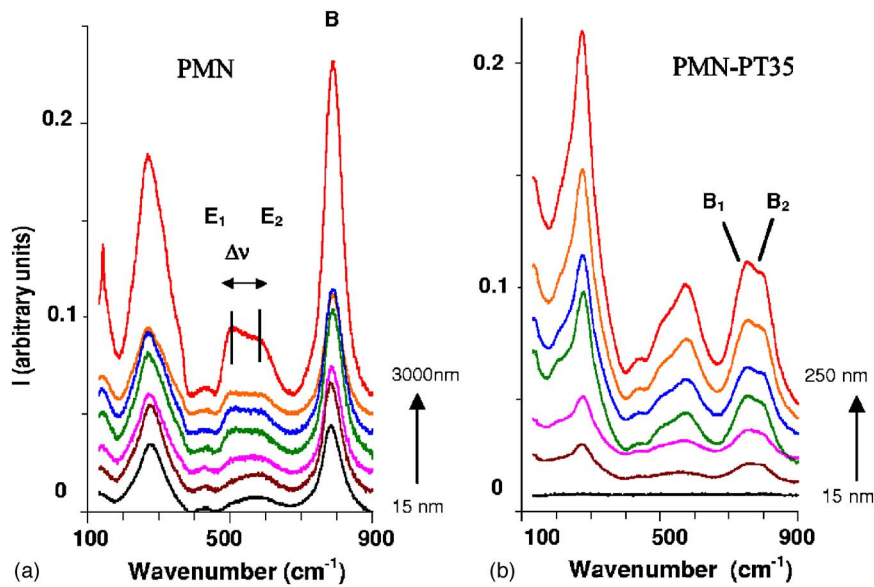
FIG. 6. (Color online) Room-temperature Raman spectra of (a) PMN (left) and (b) PMN-PT35 (right) for different grain size.

PZN-PT (see Ref. 26 by Samara, and references therein). Analogous effects with size reduction have been observed by Ziebert *et al.*[11] in thin films of $PbCaTiO_3$ grown by rf sputtering, i.e., a grain-size-induced relaxor behavior in nanocrystalline ferroelectric films below ≈ 200 nm. The interpretation given by the authors is based on "the existence of polar regions in the nanometer range due to an intrinsic disturbance of its translational symmetry."

Comparison with pressure effects in the study of PMN-PT35 is helpful. Indeed in bulk PMN-PT, the 35% of Ti compound is at the edge of a ferroelectric-relaxor crossover, as dielectric relaxation has been evidenced up to 30% of Ti content. In PMN-PT35 strong reduction of both ε_{max} and T_{max} is observed below 200-nm grain size, as well as appearance of dielectric relaxation. The supplementary cross over (below ≈ 30 nm) from relaxor to conventional cubic paraelectric phase of PMN-PT35 have not been reported (to our knowledge) in pressure experiments of lead based perovskite but is observed in doped quantum paraelectric such as $SrTiO_3$ (STO) with Ca or in the KTaNbO3 KTN.[26] Recent Raman scattering under high pressure (>10 Gpa) experiments[27] have indicated both in PMN-PT and PMN the existence of a noncubic phase, possibly rhombohedral. It should also be noticed that a spontaneous sequence (i.e., at

room pressure) of ferro-relaxor-para phases can be observed in the temperature evolution of compounds such as PSN.[28]

In the pressure study of PMN an enhancement of relaxation and of diffusivity γ as well as a strong diminution of T_{max} and ε_{max} have been reported.[26] However, size reduction shows different results: indeed an increase of T_{max} but a diminution of ε_{max} ultimately resulting in the disappearance of relaxor state with no change of diffusivity γ; moreover we have observed a diminution [Fig. 7(a)] of the 780 cm^{-1} wave number, whereas an increase is observed[28] under pressure. These results are qualitatively more reminiscent of electric field effect on relaxor state of PMN (Ref. 29) or on pressure-induced relaxor state of doped STO and KTN.

Keeping in mind these considerations a coherent and unifying picture of these phenomena stands if one considers the strain field associated to the nanosized grains. Through the picture of the spherical random bond-random field model[30] it is now well known that the existence of random electric field arising from the B cations distribution can explain the absence of long range polar order in PMN without external electric field. Furthermore elastic strain fields can also play an important part in this mechanism: this idea is quite natural
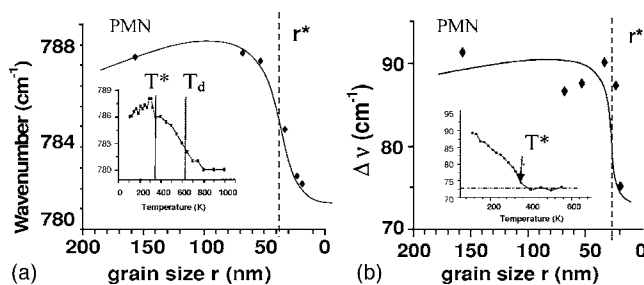

FIG. 7. Evolution with PMN grain size of (a) the overall wave number of the B band, (b) $\Delta\nu$ of the E band ; the inserts are the corresponding temperature evolutions for conventional ceramic from Ref. 19.
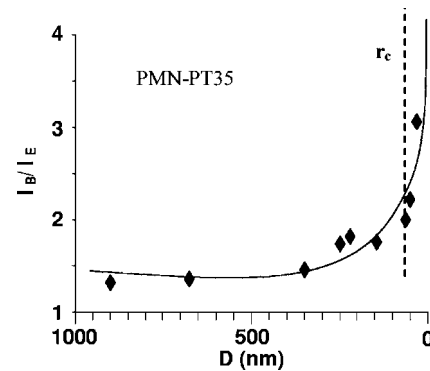

FIG. 8. Evolution with PMN-PT35 grain size of the relative intensity I_B/I_E from Raman patterns.

if one considers that these materials are highly piezoelectric/electrostrictive compounds. In Ref. 31 we have suggested that PNRs nucleate in the vicinity of chemical ordered 1:1 zone, making connection between the chemical and polar local order, the elastic compatibility between these zones and the paraelectric matrix inducing the well-known butterflylike Huang diffuse scattering observed by x-ray experiments. In this picture the desegregation or destabilization of PMN-PT35 ferroelectric macroscopic domains into PNRs and the associated appearance of dielectric relaxation, as well as in PMN the vanishing of correlations between the PNRs and the associated disappearance of relaxation are both a consequence of the modification induced by size reduction, first, to the elastic (strain) fields (direct effect) and, second, to the electric random fields (indirect effect corresponding to possible chemical redistributions).

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