

## Polarized Raman and electrical study of single crystalline titanium modified lead magnesio-niobate

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 9161

(<http://iopscience.iop.org/0953-8984/10/40/019>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.210

The article was downloaded on 14/05/2010 at 17:31

Please note that [terms and conditions apply](#).

## Polarized Raman and electrical study of single crystalline titanium modified lead magnesio-niobate

M El Marssi†, R Farhi† and Yu I Yuzyuk†‡

† Laboratoire de Physique de la Matière Condensée, Université de Picardie Jules-Verne, 33 rue Saint-Leu, 80039 Amiens, France

‡ Faculty of Physics, Rostov State University, Zorge 5, Rostov-on-Don, 344090, Russia

Received 12 June 1998, in final form 23 July 1998

**Abstract.** Raman scattering experiments were performed on the relaxor ferroelectric lead magnesio-niobate (PMN), the ferroelectric 0.8 PMN–0.2 PbTiO<sub>3</sub> (PT) and the intermediate composition 0.9 PMN–0.1 PT. In order to understand in more detail the behaviour of this series, Raman scattering spectra were also collected under dc electric field. A ferroelectric phase could be induced in the latter composition for electric fields higher than a threshold value. The behaviour of this field-induced phase was compared with the (zero-field) ferroelectric phase in 0.8 PMN–0.2 PT. Barkhausen jumps were observed in the pyroelectric current measurements, and a strong dielectric anomaly was detected in zero field heating after field cooling experiments on 0.9 PMN–0.1 PT. These results are consistent with a description of the behaviour in this series based on a cancellation of 1:1 (Mg:Nb) domain random fields by titanium ions, favouring the onset of long range ferroelectric order.

### 1. Introduction

Lead magnesio-niobate  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) is a typical relaxor ferroelectric which is known to exhibit a diffuse phase transition characterized by a strong frequency dispersion of the susceptibility, a high dielectric constant which changes very smoothly with temperature and no macroscopic spontaneous polarization.

PMN is a complex lead-based perovskite ( $\text{PbBO}_3$ ) where divalent Mg and pentavalent Nb ions are randomly distributed on the cationic B-site. The structure remains cubic at every temperature [1] with space group  $\text{O}_h^1$ , in the same way as other relaxors. But this structure is only on average, and some experiments show microscopic deviations. The existence of charged ordered regions 1:1 with rhombohedral structure and local composition  $\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_3$  has been shown from neutron and x-ray diffraction [1, 2]. Kleemann [3] suggested that these negatively charged polar regions could be considered as sources of random fields, in addition to compositional fluctuations due to the random distribution of  $\text{Mg}^{2+}$  and  $\text{Nb}^{5+}$  ions on B-sites. These random fields (RFs) inhibit the growth of ferroelectric domains, preventing any ferroelectric transition to occur in PMN. In turn, a rhombohedral ferroelectric phase can be induced by applying an external electric field, as evidenced by x-ray diffraction [4, 5] and dielectric susceptibility [3, 6] studies. This behaviour was observed in other relaxors like PLZT ceramics ( $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ ) [7–9] where the onset of a ferroelectric state under electric field at low temperature was also evidenced by Raman scattering measurements [9, 10].

Recently, many studies have focused on lead magnesio-niobate–lead titanate compounds ((1–x) PMN–x PT) due to their excellent electromechanical properties. Lead titanate (PT)

exhibits a normal ferroelectric transition at about 760 K, where the low temperature phase is tetragonal with  $C_{4v}^1$  symmetry. It has been reported that the modification of PMN with PT reduces the relaxor behaviour [11]. A small addition of PT ( $x \leq 14\%$ ) increases the value of the dielectric constant maximum and shifts the value of  $T_{max}$  to higher temperature, but the relaxor characteristics persist. Nevertheless, when the  $x$  value is greater than 14%, a rhombohedral or a tetragonal ferroelectric phase can be stabilized at low temperature. The tetragonal phase appears for large PT concentrations. A morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal phases is located in the vicinity of  $x = 0.3-0.4$  [11–13]. It has been suggested, in other works [14, 15], that a ferroelectric phase is stabilized under zero field for PT compositions as low as 10%.

The addition of  $Ti^{4+}$  ions to the PMN compound is expected to increase the disorder on the B-site, reducing subsequently the effect of polar 1:1 ordered regions. Indeed, studies on pure PMN and PMN–PT [16, 17] have shown a gradual disappearance of ordered occupation of the B-sites. Consequently, it can be concluded that Ti substitution reduces the RF, and that a long range order in PMN–PT can be achieved for large concentrations of PT.

Few studies are concerned with Raman scattering measurements on pure PMN and PMN–PT, probably due to their complex Raman spectrum [18, 19]. In spite of the centrosymmetric structure of the relaxor with  $O_h^1$  space group, a Raman spectrum exists at all temperatures. This Raman spectrum should be considered as a second order scattering process resulting from a coupling of the cubic hard phonons with the quasi-static polarization [20, 21]. This effect is related to the loss of translation symmetry due to the presence of RFs in these systems. When long range order occurs, as in the case of ferroelectric PMN–PT ( $x > 14\%$ ), second order Raman scattering transforms into first order [10].

The aim of this work is to obtain more accurate information about the rhombohedral phase which is claimed to exist in low PT concentrations of PMN–PT under electric field, and in 0.8 PMN–0.2 PT at zero field. For this purpose, Raman scattering experiments and electrical measurements were performed on oriented single crystals of  $(1 - x)$  PMN– $x$  PT with compositions  $x = 0, 0.1$  and  $0.2$ . Single crystals avoid any spurious effects which could appear in such experiments as the result of the polycrystalline state of ceramics. More specifically, Raman selection rules (RSRs) might be observed in an unambiguous way.

In the present article we report a detailed investigation of the polarized Raman spectra, as a function of temperature, for three single crystals of compositions PMN, PMN–10% PT and PMN–20% PT. The experimental conditions are reported in section 2. Section 3 will present and discuss the results. In its first part (3.1), the comparison between the results obtained in the case of these three compounds will be analysed and discussed. The second part (3.2) will be devoted to dielectric susceptibility, pyroelectric current and Raman scattering measurements under electric field on the 0.9 PMN–0.1 PT single crystal in order to contribute to the understanding of the effects of an applied electric field in these systems. Section 4 will summarize the results and conclude the article.

## 2. Experimental conditions

All samples used in this study were transparent single crystals with compositions PMN, 0.9 PMN–0.1 PT and 0.8 PMN–0.2 PT. The crystals were plates of about  $3 \times 3 \times 1.3$  mm<sup>3</sup> cut from flux grown crystals prepared at the Physics Research Institute of the Rostov State University [14]. All the samples were prepared in such a way that large faces were perpendicular to the  $\langle 100 \rangle$  direction. Before experiments under dc electric field, the 0.9 PMN–0.1 PT sample was reoriented and prepared with faces perpendicular to the  $\langle 110 \rangle$  direction. Due to the small size of the original crystals, it was not possible to obtain

single crystalline samples with faces perpendicular to the  $\langle 111 \rangle$  direction. The samples were optically polished and annealed at 850 K for half an hour in air, in order to minimize residual stresses.

For electrical measurements (dielectric susceptibility and pyroelectric current) and Raman experiments under dc electric field, the faces perpendicular to the  $\langle 110 \rangle$  direction of the 0.9 PMN-0.1 PT sample were gold electroded by sputtering. These thin film electrodes were painted with silver in order to prevent scratching of the contact by the sample holder.

Raman spectra were recorded in back scattering geometry using a Dilor Z24 triple monochromator coupled with a microscope which focused the 514.5 nm laser beam to a spot of about  $2 \mu\text{m}$  in diameter. The spectra were recorded in parallel ( $\parallel$ )  $Z(XX)\bar{Z}$  and crossed ( $\perp$ )  $Z(XY)\bar{Z}$  polarizations, where  $X$ ,  $Y$  and  $Z$  are the cubic axes.

The complex dielectric constant was measured by a Schlumberger SI 1260 impedance meter at frequencies between 10 and  $10^5$  Hz. Pyroelectric currents were obtained using a computer driven electrometer (Keithley 614). For the measurements under electric field, the 0.9 PMN-0.1 PT sample was heated up to 400 K and a dc electric field was then applied, before cooling under field down to 120 K. After having switched off the electric field, the electrodes were short-circuited and the dielectric susceptibility or the pyroelectric current was recorded while the sample was heated at a constant rate of  $4 \text{ K min}^{-1}$ . This experimental procedure will be referred to as ZFH/FC sequences (zero field heating after field cooling) in the text. Raman spectra were recorded under electric field at every temperature.

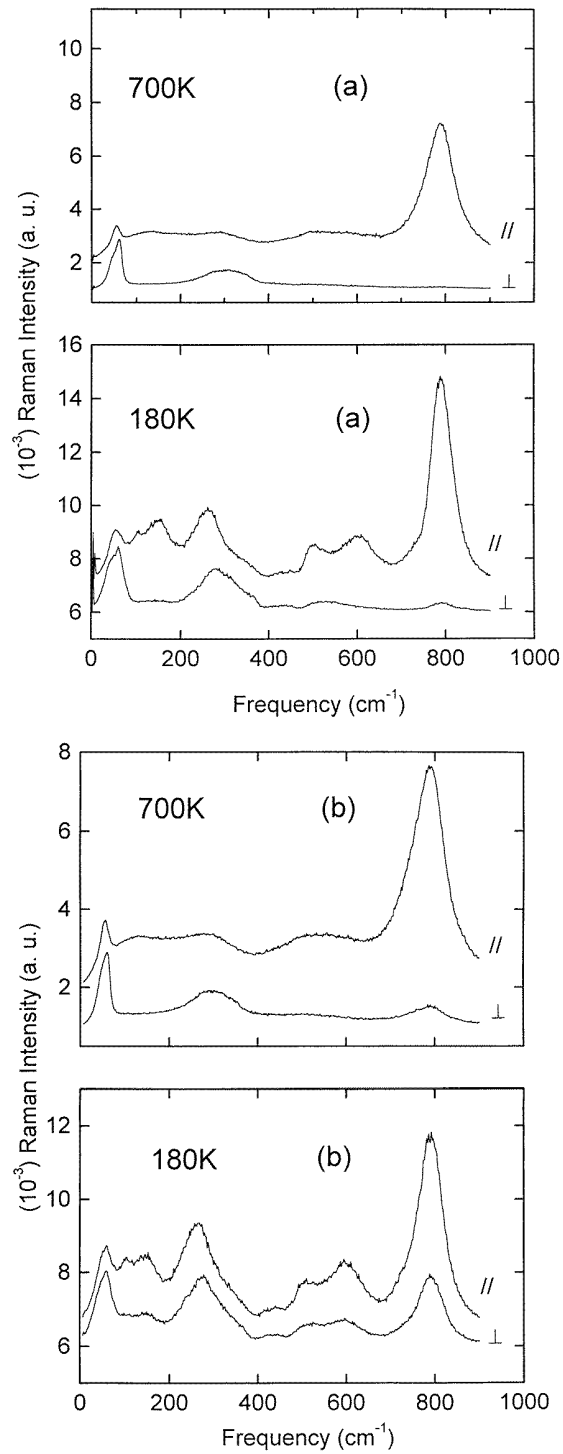
The temperature of the samples was monitored between liquid nitrogen temperature and 870 K at  $\pm 0.1$  K using a Linkam hot-stage.

### 3. Results and discussion

#### 3.1. Raman scattering from $(1-x)$ PMN- $x$ PT single crystals at zero field

The Raman spectra of pure PMN, 0.9 PMN-0.1 PT and 0.8 PMN-0.2 PT crystals recorded in parallel ( $\parallel$ ) and crossed ( $\perp$ ) polarization are presented in figure 1 at low and high temperature. All these spectra have been corrected by the population factor. Spectra were also measured at several intermediate temperatures. Note that the parallel spectra of PMN and 0.9 PMN-0.1 PT are very similar to those obtained for ceramics [18, 19].

At high temperature, the polarized Raman spectra ( $\parallel$  or  $\perp$ ) obtained for the three crystals are almost identical. As shown in figure 1, the Raman spectra in  $\parallel$  polarization exhibit a strong wide peak at high frequency ( $785 \text{ cm}^{-1}$ ) and four broad bands centred at about 54, 122, 270 and  $514 \text{ cm}^{-1}$ . A correspondence may be found, as far as the four last frequencies are concerned, with the IR spectra reported by Burns and Dacol [22]. These lines can be labelled as  $\text{TO}_1$ ,  $\text{TO}_2$ ,  $\text{TO}_3$  and  $\text{TO}_4$  from low to high frequencies. The high frequency broad line was tentatively assigned to an Nb-O-Mg stretching mode [18], but its attribution is not clear up to now. It could be a longitudinal  $\text{LO}_4$  or a higher order combination mode as well. This mode labelling was introduced by Manlief and Fan [23] and in our previous Raman studies [7, 9, 10, 20] to assign the Raman lines in the paraelectric phase of KTN and in PLZT relaxors, respectively.  $\text{TO}_1$ ,  $\text{TO}_2$  and  $\text{TO}_4$  correspond to the  $3\text{T}_{1u}$  transverse optic modes of the cubic phase ( $\text{O}_h$ ) which are normally only infrared active and  $\text{TO}_3$  corresponds to the silent mode  $\text{T}_{2u}$ . As explained in more detail in our previous article [20], these lines have to be understood as resulting from a second order Raman scattering process involving the coupling of cubic modes with the quasi-static polarization. The Raman intensity of these second order lines is proportional to the spatial correlation function of the polarization.



**Figure 1.** Parallel (//) and crossed (⊥) polarized Raman spectra obtained at 700 and 180 K for pure PMN (a), 0.9 PMN-0.1 PT (b) and 0.8 PMN-0.2 PT (c) single crystals. All the spectra have been corrected by the population factor.

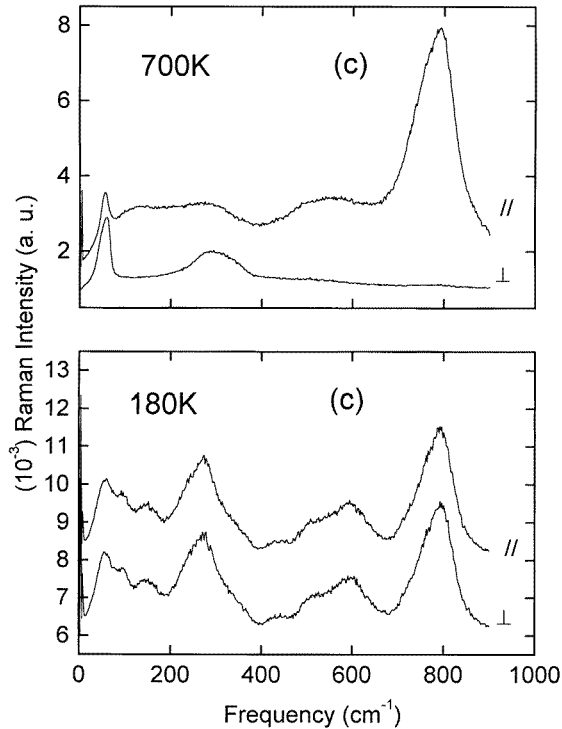
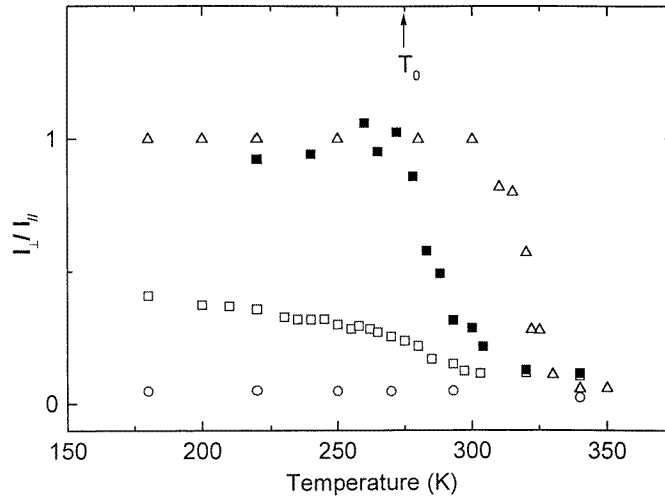


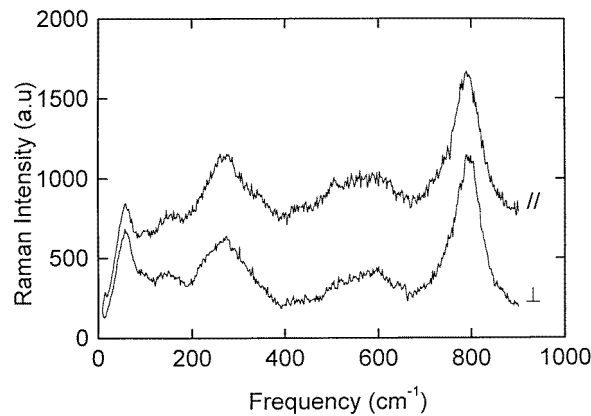
Figure 1. (Continued)

The comparison between the  $\parallel$  and  $\perp$  polarized spectra for the three compounds at high temperature shows the existence of some selection rules. Some lines appear only in  $\parallel$  polarization, and the intensity of lines in  $\parallel$  and  $\perp$  polarized spectra are very different. Such Raman selection rules (RSRs) in the average cubic phase have been explained as the result of the above mentioned second order scattering [9].

At low temperature (180 K) figure 1 shows that RSRs are enhanced in pure PMN but completely disappear in the 0.8 PMN-0.2 PT crystal, where the  $\parallel$  and  $\perp$  spectra are identical. 0.9 PMN-0.1 PT corresponds to an intermediate case, where the RSRs are less defined than in pure PMN. The loss of RSRs in 0.8 PMN-0.2 PT at low temperature can be considered as a signature of the onset of a ferroelectric long range order. This is related to the nature of the rhombohedral ferroelectric domain structure. The existence of these RSRs is more specifically evidenced by the difference in the intensity of the high frequency mode ( $\sim 785 \text{ cm}^{-1}$ ) observed in  $\parallel$  and  $\perp$  polarized spectra. Thus, in order to illustrate the evolution of the RSRs as a function of the temperature, we have reported in figure 2 the evolution of the intensity ratio  $I_{\perp}/I_{\parallel}$  against  $T$  where  $I_{\perp}$  and  $I_{\parallel}$  are the intensities of the line at  $785 \text{ cm}^{-1}$  in crossed and parallel polarizations, respectively.  $I_{\perp}/I_{\parallel}$  increases abruptly at 324 K on cooling for 0.8 PMN-0.2 PT and its value remains constant and equal to unity below this temperature. Actually, this variation of the intensity ratio corresponds to an increase of the absolute intensity of the mode in parallel polarizations and to a decrease in crossed polarizations. This temperature of 324 K coincides with the temperature determined by x-ray [24] and dielectric [14] measurements which has been attributed to the appearance of a rhombohedral ferroelectric phase in a 0.8 PMN-0.2 PT single crystal. In contrast, in the case of pure PMN where no ferroelectric transition is observed, the intensity ratio is



**Figure 2.** Raman intensity ratio  $I_{\perp}/I_{\parallel}$  of the  $785\text{ cm}^{-1}$  line as a function of the temperature for pure PMN (open circles), 0.9 PMN–0.1 PT at zero field (open squares) and under an electric field of  $2.3\text{ kV cm}^{-1}$  (full squares) and 0.8 PMN–0.2 PT (open triangles).



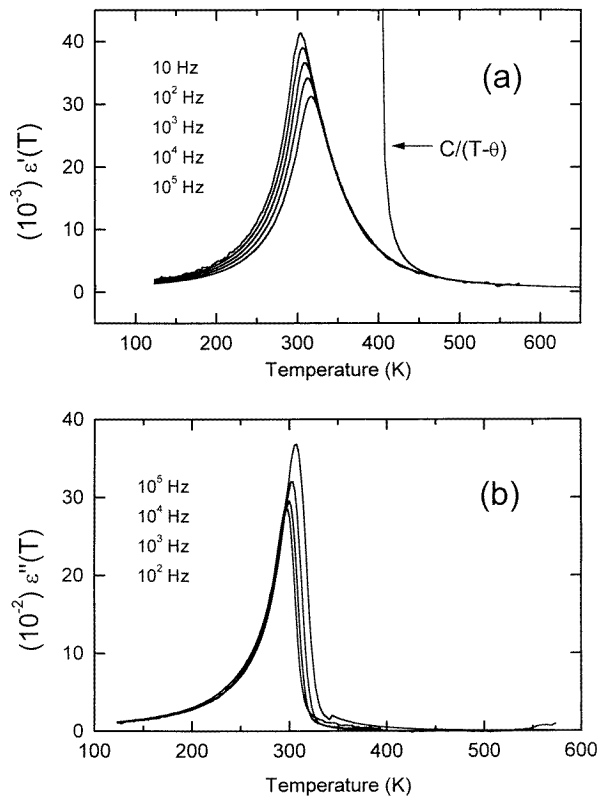
**Figure 3.** Parallel ( $\parallel$ ) and crossed ( $\perp$ ) polarized Raman spectra obtained at  $250\text{ K} (< T_0)$  for 0.9 PMN–0.1 PT under an electric field of  $2.3\text{ kV cm}^{-1}$ . The spectra have been corrected by the population factor.

close to zero at any temperature. Lastly, for the composition of 10% in PT, this intensity ratio begins to increase below about  $300\text{ K}$ , but never approaches unity at zero field. This is consistent with the lack of any macroscopic transition in the 0.9 PMN–0.1 PT crystal. Nevertheless, it shows the appearance of some ferroelectric order at  $T \leq 300\text{ K}$  which remains unachieved at low temperature.

### 3.2. Raman and electrical measurements under electric field on the 0.9 PMN–0.1 PT single crystal

Raman spectra were recorded as a function of the temperature for 0.9 PMN–0.1 PT under a dc electric field of  $2.3\text{ kV cm}^{-1}$ . Below  $T_0 \cong 275\text{ K}$ , as can be shown in figure 3 for  $250\text{ K}$ ,

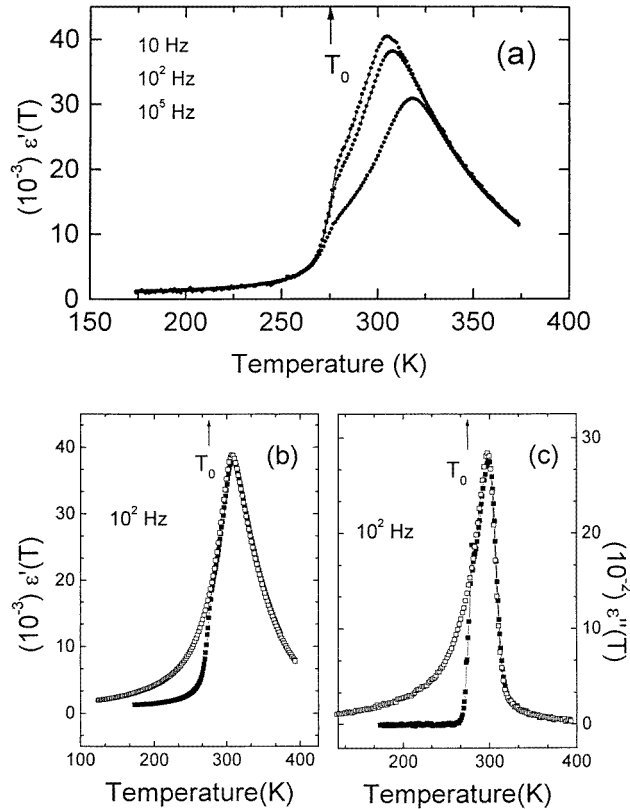
a complete lack of selection rules was observed and the intensities  $I_{\parallel}$  and  $I_{\perp}$  of all lines are the same. These facts are very similar to what is observed in the rhombohedral ferroelectric phase of the 0.8 PMN-0.2 PT crystal. Raman selection rules reappear abruptly on heating above  $T_0$ . In order to define more accurately the transition temperature, the intensity ratio  $I_{\perp}/I_{\parallel}$  was measured as a function of the temperature under electric field around  $T_0$ . The results are reported in figure 2 as full symbols. Below  $T_0$ , this ratio was constant and close to unity. A drastic variation of  $I_{\perp}/I_{\parallel}$  was observed near  $T_0$ . Above this temperature the data superimpose progressively on those obtained from the cooling experiment without dc electric field. An identical evolution of  $I_{\perp}/I_{\parallel}$  was observed in PLZT relaxor ( $x = 0.09$ ;  $y = 0.65$ ) under a dc electric field [10]. These Raman results show the possibility of inducing a ferroelectric phase below  $T_0$  in 0.9 PMN-0.1 PT under field, similar to that which exists in 0.8 PMN-0.2 PT at low temperature without field.



**Figure 4.** Real (a) and imaginary (b) parts of the dielectric susceptibility of a 0.9 PMN-0.1 PT single crystal as a function of the temperature. The labelled frequencies correspond to curves from top to bottom. At high temperature a Curie-Weiss law is obeyed with  $\theta \approx 400$  K and  $C \approx 1.7 \times 10^5$ .

Figure 4 shows the temperature dependence of the dielectric susceptibility measured at various frequencies in ZFC (or ZFH) conditions in the 0.9 PMN-0.1 PT single crystal. No anomaly is observed between 120 and 600 K, except the large dielectric dispersion typical of relaxors. The frequency dispersion and the temperature of the dielectric permittivity maximum ( $T_{max}$ ) are similar to what is observed in the case of the ceramic [11, 15]. However, the real dielectric maximum of the single crystal, for a given frequency, is



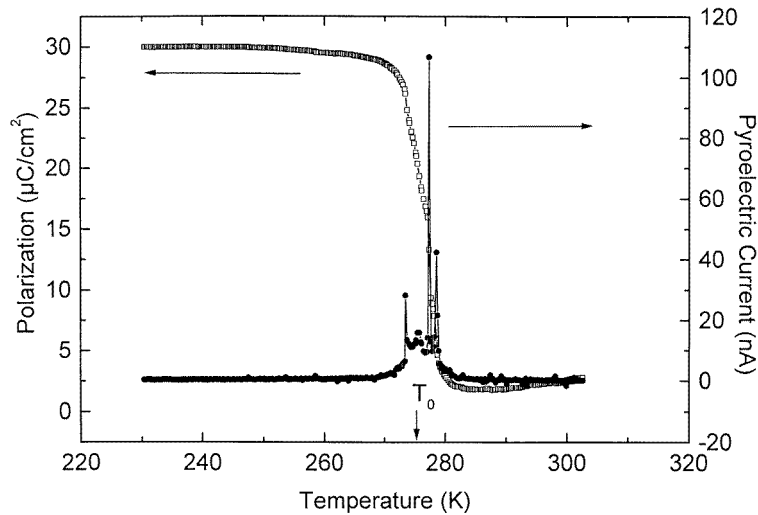


**Figure 5.** Effect of an applied electric field ( $2 \text{ kV cm}^{-1}$ ) on the real and imaginary parts of the dielectric susceptibility of a 0.9 PMN-0.1 PT single crystal as a function of the temperature. (a) Real part for three frequencies 10,  $10^2$  and  $10^5$  Hz (from top to bottom) in zero field heating after field cooling (ZFH/FC) conditions. Real (b) and imaginary (c) parts at 100 Hz in ZFH/FC conditions (full squares) and zero field heating after zero field cooling (ZFH/ZFC) conditions (open squares).

far higher. Finally, as in the case of all relaxors, at very high temperature (higher than 450 K), the dielectric susceptibility obeys a Curie-Weiss law with  $\theta \approx 400$  K and  $C \approx 1.7 \times 10^5$ . These values are very close to the ones obtained in the ceramic compound.

Dielectric measurements were also performed on the 0.9 PMN-0.1 PT crystal after cooling under a dc electric field, applied in the  $\langle 110 \rangle$  direction, for several values of the field. For a field higher than  $0.7 \text{ kV cm}^{-1}$ , a new anomaly appears in the complex dielectric permittivity at about  $T_0$ . Figure 5(a) shows the real part of the dielectric susceptibility recorded at three frequencies (10,  $10^2$  and  $10^5$  Hz) in ZFH/FC conditions for a field of  $2 \text{ kV cm}^{-1}$ . These results agree, to some extent, with the observation made by Bidault *et al* [15] in ceramics. Identical plots were obtained for low bias field (but higher than  $0.7 \text{ kV cm}^{-1}$ ). Such a steep threshold was also obtained by Colla *et al* [25] at low temperatures, i.e., below  $T_0$ , in pure PMN. The temperature at which the anomaly appears does not depend on the working frequency. Moreover, the anomaly is more pronounced when the frequency is lower. At  $T \leq T_0$ , the dielectric dispersion disappears

(figure 5(a)) and consequently the dissipative part is strongly suppressed as can be seen in the imaginary component of the susceptibility (figure 5(c)). Above  $T_0$ , the relaxor behaviour reappears and the plots superimpose on those obtained in the ZFH/ZFC experiment (see figures 5(b) and 5(c)). These dielectric data confirm the interpretation of the Raman results under dc electric field. Namely, a rhombohedral ferroelectric phase can be induced in a 0.9 PMN-0.1 PT crystal by applying an external electric field higher than the threshold value of  $0.7 \text{ kV cm}^{-1}$ . This threshold field is lower than in the case of a pure PMN single crystal [26]. It can be inferred that the threshold field necessary to induce a long range ferroelectric order at low temperature in PMN-PT relaxors decreases with increasing titanium doping.



**Figure 6.** Pyroelectric current measured in ZFH/FC conditions under an electric field of  $2 \text{ kV cm}^{-1}$  (right scale) and the corresponding polarization obtained from integration (left scale).

Another type of experiment which was performed in 0.9 PMN-0.1 PT single crystals is the depolarization current determination, from which the macroscopic polarization induced under electric field can be determined. The measurements were carried out in ZFH/FC conditions for some values of bias field applied in the  $\langle 110 \rangle$  direction. The results are reported in figure 6 for a field of  $2 \text{ kV cm}^{-1}$ . The pyroelectric current shows a large peak centred at  $T_0$ . This temperature and the intensity of the peak do not vary when the applied field decreases from 2 to  $0.7 \text{ kV cm}^{-1}$ . This confirms the dielectric measurements performed in ZFH/FC conditions. It should be pointed out that a small current is still measured around  $T_0$  for electric fields lower than  $0.7 \text{ kV cm}^{-1}$ . In addition to the large peak, some very narrow peaks are detected near the temperature  $T_0$ . Their number and temperature position vary from one experiment to another and their intensities increase with electric bias. They could be attributed to Barkhausen jumps related to domain motion when ferroelectric macrodomains transform into polar nanoregions in ZFH/FC conditions. Finally, the macroscopic polarization was obtained by integration of the pyroelectric current and is reported in figure 6. It exhibits a saturation value of  $30 \mu\text{C cm}^{-2}$  at low temperature, and decreases on crossing the depolarization temperature  $T_0$ .

The most important result obtained from these electrical and Raman experiments under electric field in 0.9 PMN–0.1 PT is the existence of the temperature  $T_0$ . It has been found in dielectric, pyroelectric current and Raman measurements. This temperature seems to correspond to the transition from a rhombohedral ferroelectric state to the relaxor state formed by polar nanoregions.

#### 4. Summary and conclusion

Raman scattering experiments have been performed on single crystals of pure PMN and  $(1-x)$  PMN– $x$  PT ( $x = 0.1, 0.2$ ). More specific attention has been paid to the 0.9 PMN–0.1 PT compound, for which, in addition, the effect of an applied dc field was investigated, including dielectric and pyroelectric current measurements.

Pure PMN is a typical relaxor ferroelectric, as well known from previous literature, and clearly observed from the Raman spectra. RSRs indeed appear at very high temperature (700 K) and persist on cooling down to 180 K. This behaviour is usually encountered in conventional relaxors, such as PLZT. It is explained by second order Raman scattering, in which hard modes are coupled with the relaxational polarization. The local breaking of symmetry associated with polar nanoregions results in the activation of normal modes belonging to irreducible representations determined by the polarization wavevector direction [9]. 0.8 PMN–0.2 PT undergoes a transition from an averaged cubic to a rhombohedral-structured ferroelectric phase [11]. RSRs are present at high temperature, but disappear on cooling below 324 K. In the cubic high temperature phase, RSRs originate from second order Raman scattering, in the same way as in pure PMN. In the ferroelectric phase, first order Raman scattering should be expected, resulting in a better definition of RSR. However, it should be stressed that eight  $\langle 111 \rangle$  directions are statistically equivalent for the spontaneous polarization in the rhombohedral phase with respect to the parent cubic phase. Therefore, a complex domain pattern takes places in this structure, and Raman lines are depolarized because of the scattering of the incident as well as the inelastically scattered light. Since first order Raman scattering exists in 0.8 PMN–0.2 PT, it would be tempting to make a symmetry attribution of the Raman lines. This cannot be performed because of the above factors. In a more general way, symmetry considerations about Raman scattering in rhombohedral compounds are hopeless except in single domain crystals.

The behaviour of the 0.9 PMN–0.1 PT compound at zero electric field lies between those of pure PMN and 0.8 PMN–0.2 PT. The onset of ferroelectric order below 300 K is better than in pure PMN, as demonstrated by the  $I_{\perp}/I_{\parallel}$  ratio which reflects, to some extent, the RSRs. Nevertheless, and in contrast to 0.8 PMN–0.2 PT, the transition to a macroscopic ferroelectric state does not occur. When applying a dc electric field, a ferroelectric phase is induced below  $T_0$  in the same way, but at weaker fields ( $\sim 0.7 \text{ kV cm}^{-1}$ ), as in PMN ( $\sim 2.2 \text{ kV cm}^{-1}$ ) [26]. This might be explained by the stronger RFs prevailing in PMN than in 0.9 PMN–0.1 PT. A threshold field characterizes the occurrence of this ferroelectric phase, i.e., this phase cannot be induced below  $0.7 \text{ kV cm}^{-1}$ . Such an effect was previously observed in PLZT [8], but the threshold in this case was smoother than in 0.9 PMN–0.1 PT, probably because of the ceramic nature of PLZT. This behaviour under electric field is also clearly seen from electrical measurements. More specifically, and as reported in section 3.2, pyroelectric current curves show sharp peaks on heating after field cooling, provided the applied field lies above the threshold. These peaks should be associated with discrete and abrupt changes in the macroscopic polarization, very likely related to domain rearrangements and domain wall motion. Such Barkhausen jumps have already been observed through birefringence measurements in pure PMN [6]. They usually characterize a multidomain state,

and are additional evidence of the ferroelectric nature of the field-induced phase below  $T_0$ .

This work was undertaken in order to compare the behaviours of titanium-modified PMN single crystals. The results have allowed us to understand in more detail the evolution from a pure relaxor compound (PMN) to 0.8 PMN-0.2 PT, in which a ferroelectric state is stable at zero field at low temperature. The relaxor behaviour of PMN is partly attributed to ordered domains in which the Mg/Nb ratio is 1:1. Because of the valencies of these cations, these domains are negatively charged and act as sources for random fields. The addition of titanium, which possesses the 'right' valency with respect to lead perovskites, balances the effect of these random fields and favours the onset of a ferroelectric long range order.

### Acknowledgments

The authors would like to thank the Région de Picardie for its financial support. Yu I Yuzyuk acknowledges financial support from ISSEP and Russian Foundation for Basic Research (projects 96-02-16219a and 96-02-16271). Permanent stimulating support from A Lebrun (INSSET, Université de Picardie) was highly appreciated.

### References

- [1] Bonneau P, Garnier P, Calvarin G, Husson E, Gavarrri J-R, Hewat A W and Morell A 1991 *J. Solid State Chem.* **91** 350
- [2] De Mathan N, Husson E, Calvarin G, Gavarrri J-R, Hewat A W and Morell A 1991 *J. Phys.: Condens. Matter* **3** 8159
- [3] Kleemann W 1993 *Int. J. Mod. Phys. B* **7** 2469
- [4] Arndt H, Sanerbier F, Schmidt G and Shebakov L A 1988 *Ferroelectrics* **79** 145
- [5] Calvarin G, Husson E and Ye Z G 1995 *Ferroelectrics* **165** 349
- [6] Westphal V, Kleemann W and Glinchuk M D 1992 *Phys. Rev. Lett.* **68** 847
- [7] Farhi R, El Marssi M, Dellis J-L, Picot J-C and Morell A 1996 *Ferroelectrics* **176** 99
- [8] Dellis J-L, El Marssi M, Tilloloy P, Farhi R and Viehland D 1997 *Ferroelectrics* **201** 167
- [9] El Marssi M, Farhi R, Dellis J-L, Glinchuk M D, Seguin L and Viehland D 1998 *J. Appl. Phys.* **83** 5371
- [10] El Marssi M, Farhi R and Viehland D 1997 *J. Appl. Phys.* **81** 355
- [11] Noblanc O, Gaucher P and Calvarin G 1996 *J. Appl. Phys.* **79** 4291
- [12] Choi S W, ShROUT T R, Jang S J and Bhalla A 1989 *Mater. Lett.* **8** 253
- [13] Ho J C, Liu K S and Lin I N 1993 *J. Mater. Sci.* **28** 4497
- [14] Emelyanov S M, Savenko F I, Trusov Yu A, Torgashev V I and Timonin P N 1993 *Phase Transitions* **45** 251
- [15] Bidault O, Licheron M, Husson E, Calvarin G and Morell A 1996 *Solid State Commun.* **98** 765
- [16] Randall C A and Bhalla A 1990 *Japan. J. Appl. Phys.* **9** 327
- [17] Hilton A D, Barber D J, Randall C A and ShROUT T R 1990 *J. Mater. Sci.* **25** 3461
- [18] Husson E, Abello L and Morell A 1990 *Mater. Res. Bull.* **25** 539
- [19] Idink H and White W B 1994 *J. Appl. Phys.* **76** 1789
- [20] El Marssi M, Farhi R, Dai X, Morell A and Viehland D 1996 *J. Appl. Phys.* **80** 1079
- [21] Di Antonio P, Vugmeister B E, Toulouse J and Boatner L A 1993 *Phys. Rev. B* **47** 5629
- [22] Burns G and Dacol F M 1983 *Solid State Commun.* **48** 853
- [23] Manlief S K and Fan H Y 1972 *Phys. Rev. B* **5** 4046
- [24] Bunia O A, Zakharchenko I N and Emelyanov S M 1993 *Izv. Ross. Akad. Nauk Ser. Fiz.* **57** 160
- [25] Colla E V, Koroleva E Yu, Nabereznov A A and Okuneva N M 1994 *Ferroelectrics* **151** 337
- [26] Ye Z G and Schmid H 1993 *Ferroelectrics* **145** 83