JOURNAL OF MATERIALS SCIENCE **41** (2006) 27–30

Polar nanoclusters in relaxors

R. BLINC[*]
J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
E-mail: robert.blinc@ijs.si

V. V. LAGUTA
J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia; Institute for Problems of Materials Science, Ukrainian Academy of Sciences, Krjijanovskogo 3, 03143 Kiev, Ukraine

B. ZALAR
J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

J. BANYS
Faculty of Physics, Vilnius University, Sauletekio al. 9, 2040 Vilnius, Lithuania

The central problem in the physics of relaxors is the nature of the polar nanoclusters. Whereas relaxors are homogeneous at high enough temperatures, polar nanoregions immersed in a neutral matrix are formed below a certain temperature T_b. This should lead to a two component system. Here we present direct microscopic evidence for the two component nature of relaxors. We show that the chemical shift perturbed ^{207}Pb NMR spectra of these systems consist of an isotropic component corresponding to a spherical glassy matrix which does not respond to an applied electric field, and an anisotropic component, corresponding to frozen out polar nanoclusters which order in a strong enough electric field, forming a ferroelectric phase. This is as well reflected in the dynamic properties where the relaxation time distribution function starts to become asymmetric with decreasing temperature and a second maximum—which is never seen in dipolar glasses and is obviously due to polar clusters—appears on further cooling. We also show that the basic difference between dipolar glasses and relaxors is the fact that polar nanoclusters can be oriented in a strong enough electric field and a ferroelectric phase can be induced. This is not the case in dipolar glasses where the response is due to single dipoles which can not be ordered by applied electric fields.

1. Introduction

The central problem in the physics of relaxors [1, 2] is the nature of the polar nanoclusters which are believed to be responsible for the multi-scale dynamics, spatial inhomogeneity and many other physical properties of these materials such as giant piezo-electricity and electrostriction [3]. Whereas relaxors are homogenous at high enough temperatures, polar nanoregions immersed in a neutral matrix should be formed below a certain temperature T_B according to Burns and Dacol [4]. This would lead to a two component system. In spite of many investigations, direct physical evidence for the existence of polar nanoregions is still lacking. Here we present direct microscopic evidence for the two component nature of relaxors. We show that the ^{207}Pb NMR spectra of these systems consist of an isotropic component corresponding to a spherical glassy matrix which does not respond to an applied electric field, and an anisotropic component, corresponding to frozen out polar nanoclusters which order in a strong enough electric field, forming a ferroelectric phase. This is as well reflected in the dynamic properties where the relaxation time distribution function $f(\tau)$ starts to become asymmetric with decreasing temperature and a second maximum—which is never seen in dipolar

---

[*] Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-5914-8

glasses and is obviously due to polar clusters—appears on further cooling in the dielectric dispersion. Cross and Viehland [5] pointed out the similarity between relaxors and dipolar glasses and suggested that nanoclusters are dynamic entities with thermally fluctuating dipole moments which freeze out at low enough temperatures. The present results demonstrate that the basic difference between relaxors and dipolar glasses is their response to applied electric fields: Polar nanoclusters—corresponding to the anisotropic component in the NMR spectra—can be oriented in a strong enough applied electric field and a ferroelectric phase can be induced. This is not the case in dipolar glasses where the response is due to single dipoles which cannot be ordered by applied electric fields.

2. Results and discussion

We have investigated a single crystal of the prototype relaxor lead manganese niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$, abbreviated as PMN. It is a perovskite solid solution characterized by site and charge disorder. The dipolar glass studied for comparison was a $(ND_4)_{0.5}$ $Rb_{0.5}D_2PO_4$ single crystal abbreviated as DRADP-50. The techniques used for PMN were field cooled and zero field cooled ^{207}Pb magnetic resonance and broad band dielectric dispersion spectroscopy. The electron paramagnetic resonance (EPR) spectra of 0.1% $Mn^{2+}+$ doped PMN ceramics were investigated as well. DRADP-50 was studied by 2D and 1D^{2}H and ^{31}P NMR and dielectric spectroscopy for comparison. A broad band dielectric dispersion study was performed on a PSN-PZN-PMN mixed system.

The macroscopic symmetry of PMN is cubic between 100 K and 4 K. At high temperatures above $T_B \approx 617$ K PMN behaves like all other simple perovskites. The dynamics of the system is determined by the soft TO phonon which exhibits a normal dispersion and is underdamped at all wave vectors. Below T_B in addition to the soft mode – which becomes overdamped [6]—a new dielectric dispersion mechanism appears at lower frequencies which can be described by a correlation time distribution function $f(\tau)$.

As it can be seen from Fig. 1a the correlation time distribution function $f(\tau)$ for PSN-PZN-PMN (obtained from broad band dielectric dispersion data) becomes asymmetric with decreasing temperature and a second maximum at long correlation times appears. Such behaviour was also observed [7] for other relaxors, such as PMN, PLZT and SBN. This second maximum is not seen in dipolar glasses like DRADP-50 (Fig. 1b). It seems to be specific to relaxors and signals the formation of polar nanoclusters. This is supported by the fact that this maximum changes if an external electric field E larger than the critical field E_C is applied along the ferroelectric [111] direction at $T < 205$ K. The first maximum of $f(\tau)$ corresponding to shorter correlation times, on the other hand, is similar to the one in the dipolar glasses and is not affected by electric fields.

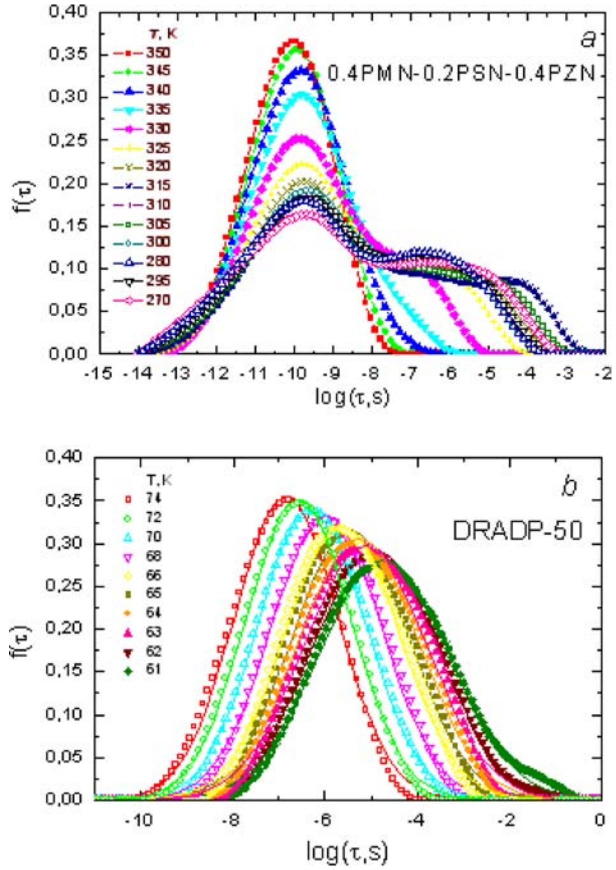

Figure 1 (a) Relaxation time distribution function $f(\tau)$ describing the dielectric dispersion in relaxor 0.4PMN-0.2PSN-0.4PZN. The short time scale maximum describes the glassy type dynamics whereas the long time scale part refers to the polar cluster dynamics. The same features are obtained in PMN, PLZT, and SBN relaxors. (b) Relaxation time distribution function in the dipolar glass DRADP-50 where the long time scale maximum is absent.

To investigate the nature of the polar nanoclusters and the surrounding glassy matrix on the microscopic level and to get spatially resolved evidence of the electric field response of PMN we performed field cooled (FC) and zero field cooled (ZFC) ^{207}Pb ($I = 1/2$) NMR experiments at different temperatures and orientations of the crystal in magnetic and electric fields. (Fig. 2a, b and c).

The ^{207}Pb spectrum at 290 K (Fig. 2a) is isotropic and of a Gaussian line shape. Two dimensional (2D) separation of interactions experiments show that the spectra are in fact frequency distributions and are composed of a large number of individual ^{207}Pb lines with different chemical shifts. This is incompatible with the assumption that the Pb ions sit at their high-symmetry cubic sites as in this case all Pb sites would be equivalent and only a single sharp line is expected. The fact that we see a Gaussian frequency distribution demonstrates that we deal with a spherical glass where all Pb nuclei are displaced but there is no preferential frozen out orientation or magnitude of displacement.

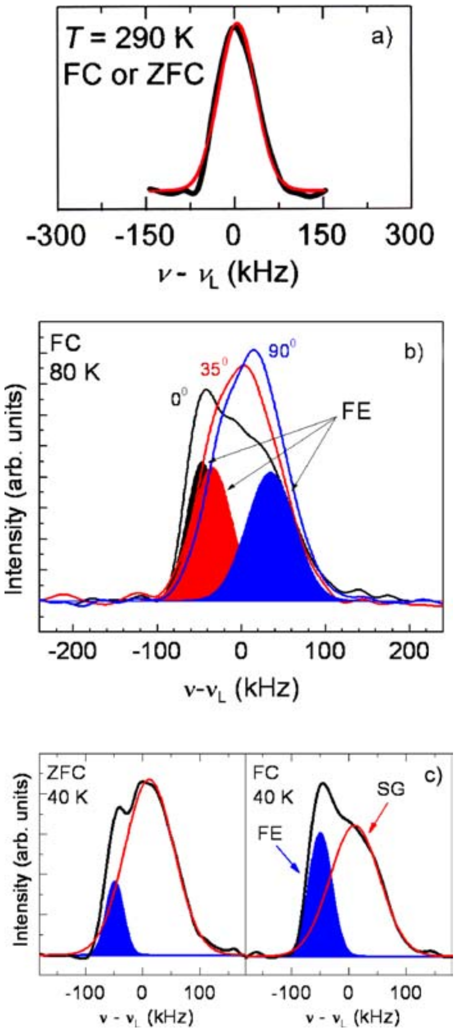

Figure 2 (a) FC and ZFC ^{207}Pb NMR spectra of PMN at 290 K. (b) FC ^{207}Pb NMR spectra of PMN at 80 K and different orientations of the crystal in the magnetic field. The spectra clearly consist of two components, an isotropic and an anisotropic one. (c) Field cooled and zero field cooled ^{207}Pb NMR spectra of PMN at 40 K showing the effect of the electric field on the concentration of the FE clusters.

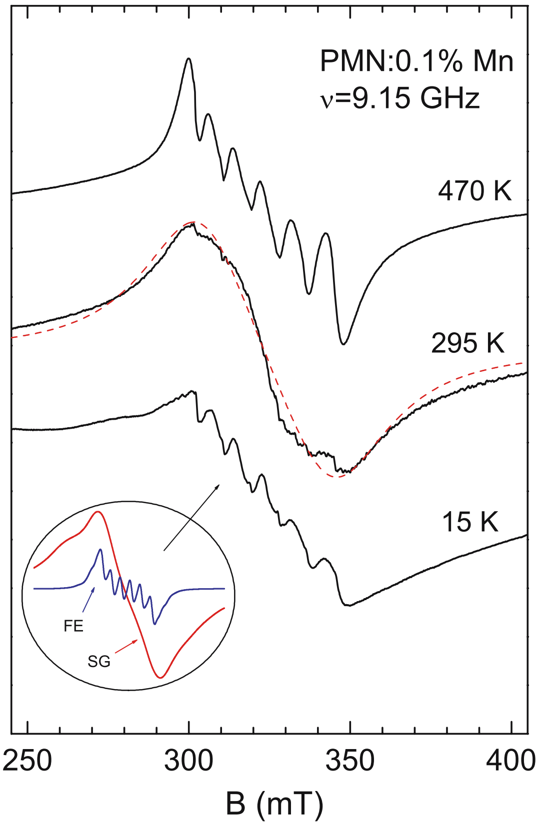

Figure 3 EPR spectra of 0.1% Mn^{2+}- doped PMN ceramics. The insert shows decomposition of the spectrum on two components, broad (SG) and narrow (FE) related, respectively, to glass matrix and ferroelectric clusters.

If the Pb ion shifts only varied in the orientation and not in magnitudes, a powder-like pattern rather than the observed Gaussian line shapes would be seen. Due to short-range order correlation among the displacements clusters are formed which fluctuate in time, orientation and magnitude of the dipole moment [4]. The orientational bias is here spherically symmetric. This agrees with the model proposed by Vakhrushev [8] which states that above the freezing temperature the displacements of the Pb nuclei lie in a spherical shell around the cubic position as well as with the mezoscopic spherical random bond–random field (SRBRF) model [9]. At lower temperatures an anisotropic component appears in the ^{207}Pb NMR spectrum in addition to the isotropic one (Fig. 2b). Its angular dependence in the external magnetic field follows the $(3\cos^2\vartheta - 1)$ law. The anisotropic component—which is itself a frequency distribution—corresponds to polar clusters frozen out on the NMR time scale and oriented along the ferroelectric [111] axis. Such a two component line shape is not seen in dipolar glasses [10].

As it can be seen from Fig. 2c, the anisotropic frozen polar cluster component increases in intensity if the crystal is cooled at low enough temperatures in an electric field larger than the critical field and applied along the [111] direction. A transition to the ferroelectric phase is induced for $E > E_C$. The difference between FC and ZFC Pb NMR spectra is striking and shows the existence of a two-component behavior—the spherical glassy matrix and the ferroelectric clusters—on a microscopic level. According to the intensities of the NMR lines, about 50% of the Pb nuclei still reside in the spherical glass matrix which does not respond to the electric field and 50% in the ferroelectric polar clusters which respond to electric fields. It should be noted that below $T_C = 210$ K a sudden increase in the intensity of the anisotropic component is also seen in the ZFC spectra, but the increase in the intensity of the anisotropic component is two times smaller then in the FC spectra at the same temperature. This shows that PMN is an incipient ferroelectric [11] and that in the absence of the electric field the concentration of the polar clusters is below the threshold for a percolation type ferroelectric transition. Electric fields did not change the NMR spectra of the dipolar glass DRADP-50 and no difference between field cooled and zero field cooled spectra could be detected [9]. The two component nature of the relaxor state is also seen in the EPR spectra of 0.1% Mn^{2+} doped PMN ceramics. Here the Mn^{2+} ions substitute for Mg^{2+} and the isotropic electron-nuclear hyperfine coupling with ^{55}Mn ($I = 5/2$) serves as a microscopic probe of the local structure [12]. At room temperature the Mn^{2+} EPR spectrum consists of a broad $1/2 \rightarrow -1/2$ line with completely unresolved ^{55}Mn nuclear hyperfine structure (Fig. 3). This is due to a distribution of ionic shifts from cubic positions which vary both in direction and magnitude [11].

On the EPR time scale 10^{-9} s these ionic displacements are static at room temperature, resulting in a broad unresolved line. When the temperature increases to 410–470 K, the line shape changes and six well resolved ^{55}Mn isotropic hyperfine lines appear. The sharp lines in the spectrum correspond to the motional narrowing regime where the fluctuations of the ionic displacements become fast on the EPR time scale. Thus PMN at 470 K indeed corresponds to a system of randomly oriented non-cubic clusters which fluctuate in time, direction and value of local polarizations, i.e. to a dynamic spherical glass [9, 11]. Below 40–50 K another transformation occurs. Well resolved ^{55}Mn hyperfine lines appear again but are now accompanied by a broad (75–80 mT) line. This demonstrates that in addition to the frozen out spherical glass matrix large nearly ordered ferroelectric domain like polar clusters exist where the distribution of off-center ionic shifts is rather narrow allowing for the appearance of sharp hyperfine lines. Such a narrowing has been seen in the anisotropic component of the Pb NMR spectra too.

We have thus for the first time observed separately the anisotropic ferroelectric like polar clusters, which respond to an external electric field, and the isotropic spherical glass matrix into which the polar clusters are embedded, and which is not affected by electric fields. We have as well observed separately the different dynamics of these two entities. This represents a microscopic confirmation of the two component model of relaxors first proposed by Burns and Dacol [4]. Our results also show that the basic difference between relaxors and dipolar glasses is that due to the existence of polar clusters relaxors respond to an external electric field and a ferroelectric phase can be induced whereas this is not the case for dipolar glasses where the response is due to single dipoles. Relaxors exhibit polar cluster disorder on the nanometric scale. They are thus indeed intermediate between ferroelectrics where domain disorder exists on the macroscopic scale and dipolar glasses, where disorder exists on the atomic scale.

References

1. G. A. SMOLENKSY, *J. Phys. Soc. Jpn. (Suppl.)* **28** (1970) 26.
2. L. E. CROSS, *Ferroelectrics* **76** (1987) 241.
3. H. FU and R. E. COHEN, *Nature* **403** (2000) 281.
4. G. BURNS and F. H. DACOL, *Phys. Rev. B* **28** (1983) 2527.
5. D. VIEHLAND, J. F. LI, S. J. JANG, L. E. CROSS, and M. WUTTIG, *Phys. Rev. B* **43** (1991) 8316.
6. T. EGAMI, E. MAMONTOV, W. DOMOWSKI, and S. B. VAKHRUSHEV, in "Fundamental Physics of Ferroelectrics," edited by P. K. Davies and D. J. Singh, *American Institute of Physics*, CP **677** (2003) 48.
7. J. BANYS, unpublished work from this laboratory.
8. S. B. VAKHRUSHEV and N. M. OKUNEVA, *AIP Conf. Proc.* **626** (2002) 117.
9. R. PIRC and R. BLINC, *Phys. Rev. B* **60** (1999) 13470.
10. R. BLINC *et al., Phys. Rev. Lett.* **63** (1989) 2248.
11. R. BLINC, V. V. LAGUTA and B. ZALAR, *Phys. Rev. Lett* **91** (2003) 247601.
12. R. BÖTTCHER *et al., Phys. Rev. B* **62** (2000) 2085.