

# Solid-state single and triple-quantum $^{93}\text{Nb}$ MAS NMR studies of ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and a related pyrochlore

Luísa P. Cruz <sup>a,b</sup>, João Rocha <sup>a,\*</sup>, Júlio D. Pedrosa de Jesus <sup>a</sup>, Jean M. Savariault <sup>c</sup>,  
Jean Galy <sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Aveiro, 3810 Aveiro, Portugal

<sup>b</sup> Polytechnic Institute of Viseu, 3510 Viseu, Portugal

<sup>c</sup> Centre d'Elaboration de Materiaux et d'Etudes Structurales, CNRS B.P. 4347 Toulouse, France

## Abstract

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN), a well-known relaxor ferroelectric material, and a related pyrochlore phase have been studied by single- and triple-quantum  $^{93}\text{Nb}$  MAS NMR spectroscopy. The assignment of the NMR resonances has been attempted. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** PMN; ferroelectric material; MAS NMR spectroscopy

## 1. Introduction

Lead magnesium niobate,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN), is a well-known relaxor ferroelectric material with a high dielectric constant and electrostrictive coefficient exhibiting a diffuse phase transition (broad Curie peak in the range of the ferroelectric–paraelectric phase transition). Hence, PMN displays great potential for being used in, among others, multilayer ceramic capacitors, electrostrictive actuators and materials for optoelectronics. At room temperature, PMN has the cubic perovskite structure, space group  $Pm3m$ ,  $a = 4.04$  Å. During the synthesis of PMN, pyrochlore phases (space group  $Fd3m$ ,

$a = 10.60$  Å) often form, deteriorating the ferroelectric properties of the material [1–3].

Here, we wish to report  $^{93}\text{Nb}$  MAS NMR studies of PMN and pyrochlore.  $^{93}\text{Nb}$  is a spin 9/2 quadrupolar nucleus with a relatively large nuclear quadrupole moment ( $-0.22 \times 10^{28}$  Qm<sup>-2</sup>) and 100% natural abundance. In the solid state, any electric field gradients created by the electronic cloud at the nucleus interact with the nuclear electric quadrupole, giving rise to considerable broadening of the spectral lines and making  $^{93}\text{Nb}$  a difficult nucleus to study. In this work, we have used very fast MAS, up to 32 kHz, and the recently introduced technique for the study of half-integer quadrupole nuclei in solids, multiple-quantum (MQ) MAS NMR spectroscopy [4]. Apart from a brief reference to lithium niobate [5], this is the first MQ MAS NMR study of a spin 9/2 nucleus.

\* Corresponding author. Tel.: +351-34-370730; fax: +351-34-370084; e-mail: rocha@dq.ua.pt

## 2. Experimental

### 2.1. Samples

Pyrochlore was prepared by the conventional mixed oxides method [6,7] and PMN by the columbite method [7]. In the former, stoichiometric amounts of reagent grade PbO (yellow, Merck 99% pure), MgO (BDH 93.3% light) and crystal grade Nb<sub>2</sub>O<sub>5</sub> (Aldrich, 99.9% pure) were mixed and wet ball-milled in ethanol for 12 h. The resultant wet slurry was dried and calcined in a closed alumina crucible at 750°C for 4 h. The columbite method consists of two steps. Firstly, columbite, MgNb<sub>2</sub>O<sub>6</sub>, is prepared from a mixture with composition 1.72 mol MgO: 1.0 mol Nb<sub>2</sub>O<sub>5</sub>. After ball-milling in ethanol for 12 h and drying, this mixture was calcined in an alumina crucible at 1100°C for 6 h. The columbite obtained was ball-milled with PbO and calcined in a close alumina crucible at 850°C for 4 h.

### 2.2. Techniques

<sup>93</sup>Nb MAS NMR spectra were recorded at 97.84 MHz on a (9.4 T) Bruker MSL 400P spectrometer. Single-quantum <sup>93</sup>Nb MAS NMR spectra were measured using short and powerful radio-frequency pulses (0.6 μs, equivalent to a 6° pulse angle), a 32 kHz spinning rate (2.5 mm Bruker double-bearing probe) and a recycle delay of 400 ms. Chemical shifts are quoted in ppm from solid Nb<sub>2</sub>O<sub>5</sub>. The triple-quantum (3Q) <sup>93</sup>Nb MAS NMR spectra were recorded on a 4 mm Bruker double-bearing probe with a spinning rate of 14 kHz and a radio-frequency magnetic field amplitude of ca. 132 kHz. Although the much stronger radio-frequency fields (in excess of 250 kHz) available with the 2.5 mm Bruker probe are desirable when carrying out MQ MAS experiments, it was found that the small amount of sample used did not afford an acceptable signal-to-noise ratio. A total of 128 data points were acquired in the *t*<sub>1</sub> dimension in increments of 2 and 6 μs for PMN and 6 μs for pyrochlore. To produce pure-absorption line shapes in the 3Q MAS spectra the optimum conditions for excitation and transfer of the (±3Q) coherences using a simple two-pulse sequence were used [8]. Recording a good quality 3Q MAS NMR spectrum is particularly difficult for a spin 9/2

nucleus [5]. The first and (in particular) the second pulse flip angles were optimised on the very samples examined and found to be 81 and 31° close to the values calculated numerically (respectively, 90 and 35°) [5]. The phase cycling was composed of six phases for the selection of 3Q coherences. This phase cycling was combined with a classic overall four-phase cycle in order to minimise phase and amplitude mis-settings of the receiver. A total of 3024 transients were recorded with a recycle delay of 400 ms. The total acquisition time was over 40 h for each two-dimensional spectrum. The ppm scale was referenced to *v*<sub>0</sub> frequency in the *v*<sub>2</sub> domain and to 3 *v*<sub>0</sub> in the *v*<sub>1</sub> domain [reference solid Nb<sub>2</sub>O<sub>5</sub>].

## 3. Results and discussion

Fig. 1 shows central (*m* = +1/2 ↔ *m* = −1/2) transition single-quantum <sup>93</sup>Nb MAS NMR spectra of PMN and pyrochlore. PMN gives a relatively broad peak at 218 ppm and a sharp resonance at 320 ppm. The pyrochlore spectrum contains a single asymmetric peak at 214 ppm.

The <sup>93</sup>Nb 3Q MAS NMR spectrum of PMN (Fig. 2) confirms that this material contains only two distinct niobium environments. Peak S1 is given by a site with a large quadrupole coupling constant (*C*<sub>Q</sub>), in excess of 20 MHz, and it displays strong spinning side bands along F1. Due to the large *C*<sub>Q</sub>, this peak is much fainter than S2. The quantification of MQ MAS NMR spectra is not a trivial problem. Indeed, the intensity of the resonances is not representative of the actual concentration of the species because the

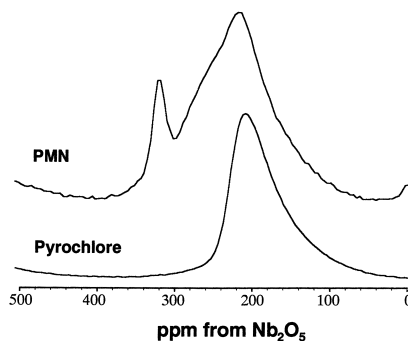


Fig. 1. Central transition <sup>93</sup>Nb MAS NMR spectra of PMN and pyrochlore.

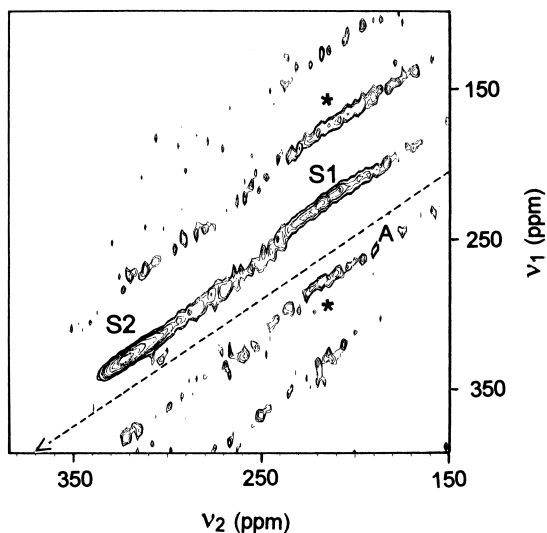


Fig. 2.  $^{93}\text{Nb}$  3Q MAS NMR spectrum of PMN. Asterisks depict spinning side bands.

excitation of MQ coherences is strongly dependent on  $C_Q$ . Hence, to estimate the relative intensities of S1 and S2, we have resorted to the simulation of the full (central and satellite transitions)  $^{93}\text{Nb}$  MAS NMR spectrum of PMN (Fig. 3). A S1/S2 intensity ratio of ca. 9.5 was found. In addition, the following values were obtained for, respectively, S1 and S2: isotropic chemical shifts of 302 and 320 ppm,  $C_Q$  of 21.5 and 8.5 MHz, and asymmetry parameters of 0.8 and 0.5.

The simulation of the full  $^{93}\text{Nb}$  MAS NMR spectrum of pyrochlore (Fig. 4) is more difficult. While

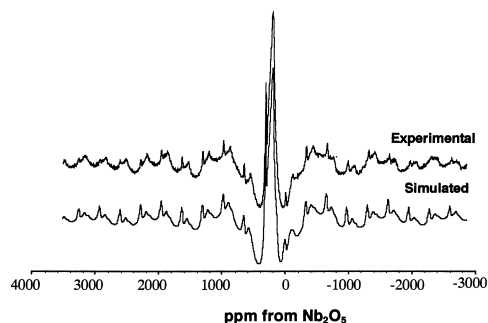


Fig. 3. Expanded region of the full (central and satellite transitions) experimental and simulated  $^{93}\text{Nb}$  MAS NMR spectra of PMN.

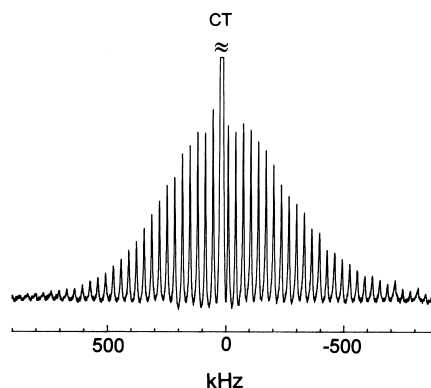


Fig. 4. Full experimental  $^{93}\text{Nb}$  MAS NMR spectrum of pyrochlore. CT denotes the central transition line; the spinning side bands are caused by the satellite transitions.

the central transition spectrum (Fig. 1) exhibits a long low-frequency tail and could not be simulated with only one peak, the 3Q MAS NMR spectrum (Fig. 5a) shows the presence of a single resonance. Close examination of this spectrum (Fig. 5b) suggests the presence of a distribution of isotropic chemical shifts and quadrupole couplings: although P1 is essentially located on the anisotropic axis 'A', the peak is broadened along 'CS' and 'QIS', the axes giving the direction of, respectively, the isotropic chemical shifts and the induced quadrupole shifts [5]. It has been previously reported that when such distributions are present, the MAS NMR central transition lines of glasses and disordered materials often display a tail at low frequency and, in addition, the satellite transitions spinning side bands envelop is approximately Gaussian [9]. This last effect is, indeed, seen in the full  $^{93}\text{Nb}$  MAS NMR spectrum of pyrochlore (Fig. 4).

We now attempt to rationalise the NMR evidence. In pyrochlore and PMN (Fig. 6) niobium is in octahedral coordination. The Nb–O distance is slightly shorter in the former, 1.96 and 2.02 Å, respectively. Hence, the two solids are expected to give  $^{93}\text{Nb}$  NMR resonances with different isotropic chemical shifts and quadrupole parameters. In addition, the NMR parameters, particularly  $C_Q$ , are likely to be determined by atoms in the second, third and other shells further away from the  $^{93}\text{Nb}$  nucleus. The second pyrochlore and PMN shells are different. In the latter, eight lead atoms produce a cubic environ-

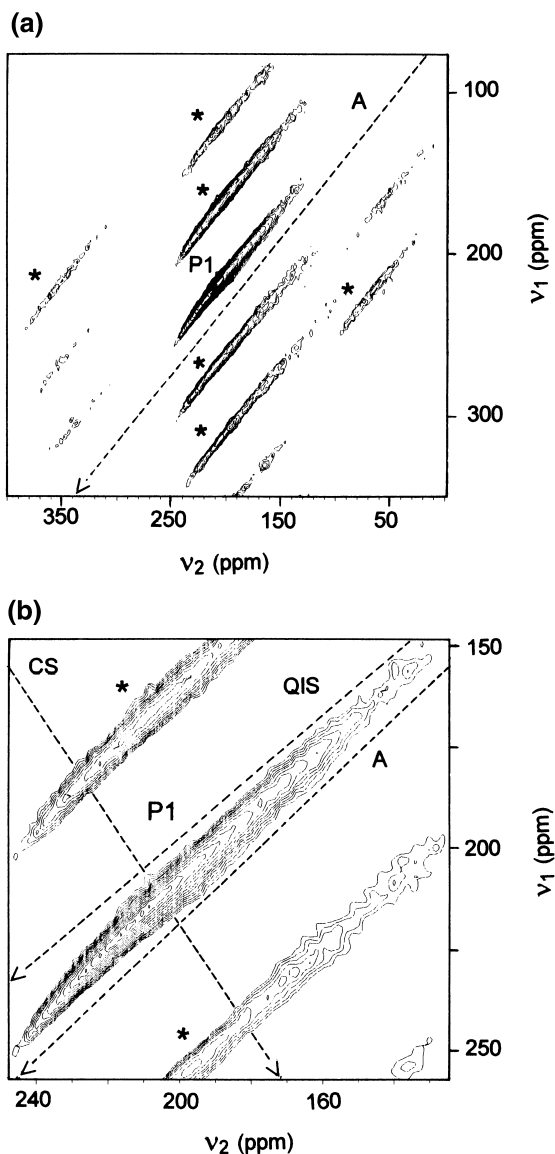


Fig. 5. (a)  $^{93}\text{Nb}$  3Q MAS NMR spectrum of pyrochlore; (b) shows an expanded region of the spectrum. Asterisks depict spinning side bands.

ment while in the pyrochlore structure there are only a maximum of six lead atoms in an equatorial plane. This, however, cannot explain the two resonances given by PMN.

Looking further away, at the third shell Nb... (Nb,Mg), one finds that in both solids each  $\text{NbO}_6$  octahedron is surrounded by six octahedra. However,

the shape of each surrounding is octahedral in PMN and pyrochlore has a three-fold axial geometry. In a  $\text{Pb}_2(\text{Mg}_{2/3}, \text{Nb}_{4/3})\text{O}_6$  perovskite there are two possible ways of filling in the six octahedra: (i) 3  $\text{NbO}_6$  and 3  $\text{MgO}_6$ ; (ii) 4  $\text{NbO}_6$  and 2  $\text{MgO}_6$ . These two kinds of surroundings might explain the two  $^{93}\text{Nb}$  NMR PMN resonances observed. If so, the two resonances should be in a 1:2 intensity ratio. However, the spectral simulations of pure PMN reveal a completely different (1:9.5) peak intensity ratio. A different assignment for the resonances has, thus, to be found.

TEM studies have previously shown that PMN contains regions which exhibit 1:1 ordering of the B-site cations [10,11]. These regions are surrounded by a niobium-rich 'sea' (Fig. 7). In order to maintain charge neutrality in such regions, the lattice must contain compensating charged point defects [12]. Within the 1:1 ordered regions oxygen vacancies are favoured while in the 'sea' lead vacancies form. As a tentative attribution of the two PMN  $^{93}\text{Nb}$  NMR resonances, we suggest that they are given by (i) niobium in regions exhibiting 1:1 ordering of B-site cations (peak at 320 ppm) and (ii) niobium in the 'sea' environment (peak at 218 ppm). If so,  $^{93}\text{Nb}$  NMR provides a simple and direct way of quantifying the two regions.

Pyrochlore compounds can be described using the formulae  $\text{AB}_2\text{O}_6$  or  $(\text{A}_2\text{O}')\text{B}_2\text{O}_6$ . In each case, the skeleton is made out of blocks of four  $\text{BO}_6$  octahedra sharing corners and building up a super-tetrahedron, every single tetrahedron sharing an octahedron (Fig. 6b). This gives rise to tunnels which run along the [110], [101] and [011] directions. At the intersection of these tunnels, large cavities appear (centred on site 8b) in the centre of which are located the A ions of the  $\text{AB}_2\text{O}_6$  type pyrochlore or the O' atom of  $(\text{A}_2\text{O}')\text{B}_2\text{O}_6$  type pyrochlore. Between the cavities, in the centre of the tunnel (site 16d) sit the A atoms of  $(\text{A}_2\text{O}')\text{B}_2\text{O}_6$  pyrochlore. A mixture of both pyrochlore types is possible provided that the total occupancy of site 8b by the A or O' atoms does not exceed 1. The corresponding formula is  $[\text{A}_x(\text{A}_2\text{O}')_{1-x}]\text{B}_2\text{O}_6$ . For the pyrochlore compound studied here, the formula becomes:  $\text{Pb}_{2-x}[\text{Nb}_{2-y}\text{Mg}_y]\text{O}_{6+(1-x-3/2y)}$ . The PMN perovskite-type compound appears to be the limit of this formula:  $x = 0$  and  $1 - x - 3/2y = 0 \Rightarrow y = 2/3$ .

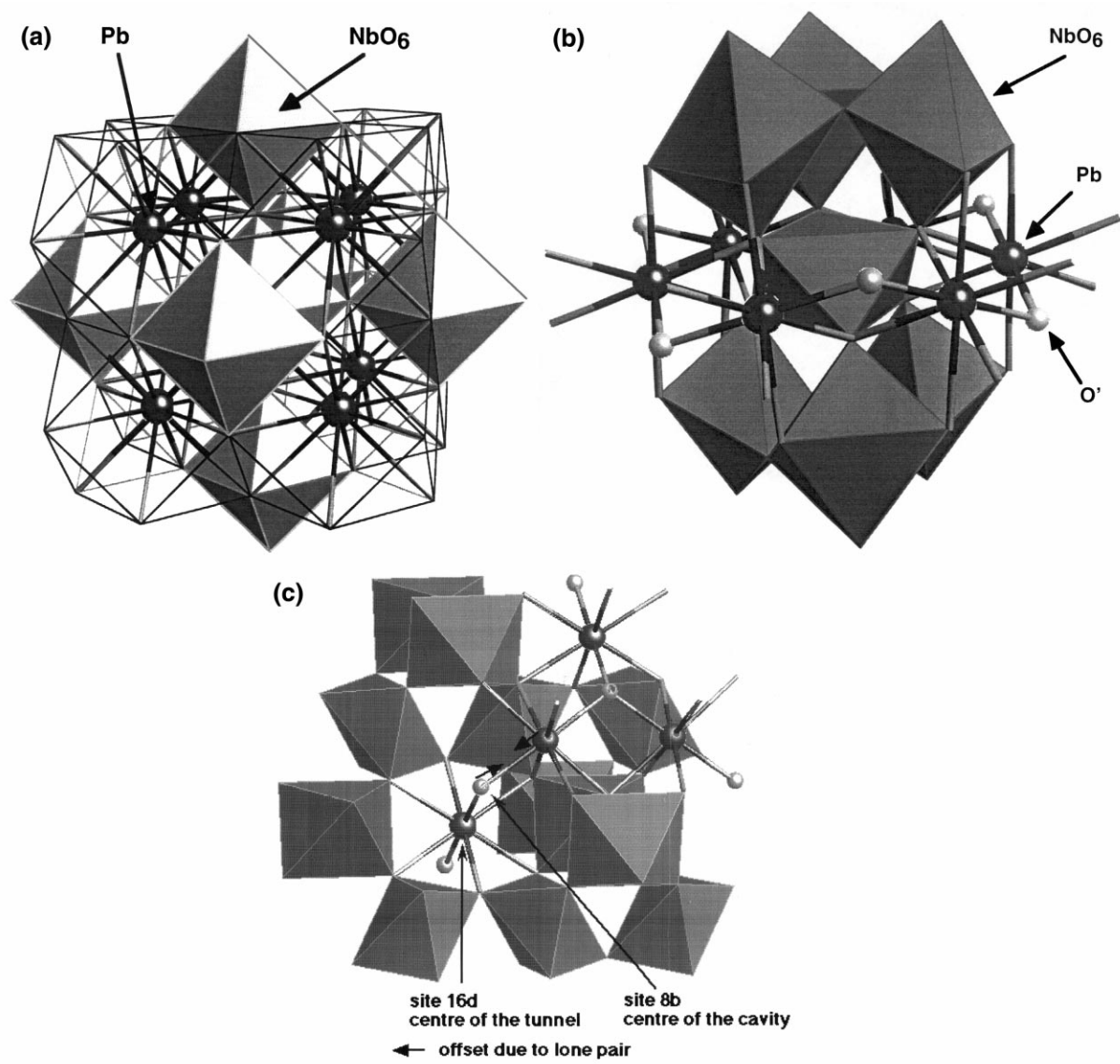


Fig. 6. Structures of (a) PMN and (b), (c) pyrochlore. Because Pb(II) bears a lone electron pair, it is shifted away from the cavity centre to the centre of the tunnel. This is illustrated in (c).

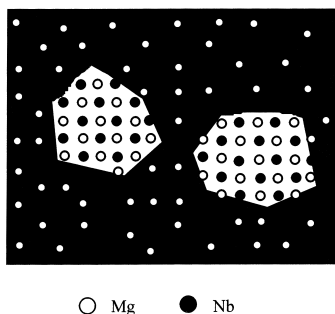


Fig. 7. PMN nanostructure showing regions with 1:1 ordering of the B-site cations [12].

Such a formula accepts variations of composition and shows why pyrochlore is a by-product of the reaction. The composition of the prepared pyrochlore,  $\text{Pb}_{1.83}[\text{Nb}_{1.71}\text{Mg}_{0.29}]\text{O}_{6.39}$ , follows this formula using  $x = 0.17$  and  $y = 0.29$  and, hence, sites 8b and 16d are partially occupied by Pb (0.17 and 0.83, respectively). The second Nb coordination sphere involves two types of surroundings according to the occupation of the Pb sites and two  $^{93}\text{Nb}$  NMR signals may, in principle, be observed. However, the crucial point here is that Pb(II) bears a lone electron pair and it is shifted away from the cavity centre by ca.  $0.86 \text{ \AA}$  [13]. Most likely, the Pb ion shifts from the centre of the cavity towards the centre of the tunnel (Fig. 6c). A Pb ion in site 8b will be shifted towards the 16d site. Hence, the Pb surrounding of Nb becomes more homogeneous: the Pb coordinates in site 8b are (0.423, 0.423, 0.423) while the coordinates of Pb in site 16d are (0.452, 0.452, 0.452); the Nb–Pb(8b) distance decreases from 4.39 to  $4.00 \text{ \AA}$  while the Nb–Pb(16d) distance increases from 3.75 to  $3.85 \text{ \AA}$ . As a result, the two possible  $^{93}\text{Nb}$  NMR resonances merge into a single broad peak. Since the

signal intensity is proportional to the population of atoms in a given site, the highest (high-frequency) side of the NMR peak is probably given by Nb local environments with every nearest Pb in site 16d. The lowest (low-frequency) side of the NMR peak is given by Nb environments with Pb in site 8d. The observed distribution of  $^{93}\text{Nb}$  NMR isotropic shifts and quadrupole couplings probably reflects the disorder in the Nb surroundings between the two Pb extreme situations.

## Acknowledgements

We thank PRODEP, PRAXIS, FEDER for financial support.

## References

- [1] S.L. Swartz, T.R. Shrout, *Mater. Res. Bull.* 17 (1982) 1245.
- [2] M. Inada, *Jap. Natl. Tech. Rep.* 27 (1977) 95.
- [3] M. Lejeune, J.P. Boilot, *Ceram. Int.* 8 (1982) 99.
- [4] A. Medek, J.S. Harwood, L. Frydman, *J. Am. Chem. Soc.* 117 (1995) 12779.
- [5] J.-P. Amoureux, C. Fernandez, *Solid State Nucl. Magn. Reson.* 10 (1998) 211.
- [6] S.L. Swartz, T.R. Shrout, *Mater. Res. Bull.* 17 (1982) 1245.
- [7] T.R. Shrout, S.L. Swartz, *Mater. Res. Bull.* 18 (1983) 663.
- [8] C. Fernandez, J.P. Amoureux, *Chem. Phys. Lett.* 242 (1995) 449.
- [9] C. Jäger, G. Kunath, P. Losso, G. Scheler, *Solid State Nucl. Magn. Reson.* 2 (1993) 73.
- [10] J. Chen, H.M. Chan, M.P. Harmer, *J. Am. Ceram. Soc.* 72 (1989) 593.
- [11] E. Husson, L. Abello, A. Morel, *Mater. Res. Bull.* 25 (1990) 539.
- [12] T.R. Shrout, W. Huebner, C.A. Randall, A.D. Hilton, *Ferroelectrics* 93 (1989) 361.
- [13] J. Galy, G. Meunier, S. Andersson, A. Åström, *J. Solid State Chem.* 13 (1975) 142.