

The properties of the non-stoichiometric ceramics $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-(x)\text{PbTiO}_3$

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Abstract

$(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-(x)\text{PbTiO}_3$ i.e. $(1-x)\text{PMN}-(x)\text{PT}$ ceramics with $x \leq 0.15$ have been obtained and investigated. With increasing x the temperature T_m increases, at which dielectric permittivity reaches its maximum (ϵ_m), increases the value of ϵ_m and decreases the degree of the diffuse phase transition. For $x \leq 0.075$ dominates electrostrictive mechanism while for $x > 0.075$ piezoelectric effect gives a contribution into electromechanical deformation of the samples. Special attention is paid to the problem of nonstoichiometry (excess and deficit of PbO and excess of MgO). © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Phase transitions in relaxor ceramics are important from both theoretical and practical points of view.^{1–4} In particular, lead magnesium niobate (PMN)-related materials have been extensively studied in recent years.^{1–6} However, up to now all aspects of polarization behaviour of PMN-based compounds have not been clearly understood. The maximum value of dielectric permittivity in pure PMN is placed at temperature $T_m \approx 264$ K (lower than the room temperature). Addition of PbTiO_3 (PT)^{5,7,8} shifts T_m towards higher temperatures, and changes dielectric and electromechanical parameters and degree of diffuse phase transition. PMN–PT solid solutions exhibit many properties important for dielectric, electrostrictive and microwave applications.^{9,10}

Experimental results on dielectric and electrostrictive properties of PMN–PT are often contradictory even when reported by the same authors. It may be a result of synthesis process during which except perovskite phase also the pyrochlore phase arrives. Pyrochlore phase worsens the dielectric and electrostrictive properties. Contradictory conclusions concerning the relations between x , T_m , ϵ_m , and hysteresis of electromechanical deformation can also be found in the literature.^{11–17}

In this study we explain the problems as mentioned above and the influence of conditions and non-stoichiometry on the structure and dielectric and electromechanical parameters of PMN–PT are presented.

2. Samples and experiment

$(1-x)\text{PMN}-(x)\text{PT}$ ($x = 0, 0.025, 0.05, 0.10, 0.125, 0.15$) ceramic samples have been obtained from columbite precursors¹⁷ by two methods—(1) conventional sintering (CS) and (2) hot pressing (HP). The columbite (MgNb_2O_6) has been synthesized with a small excess of MgO and then after addition PbO and TiO_2 powders have been mixed and sintered at 973 K. In the CS method the final temperature of sintering was $T_s = 1533$ K, the time $t_s = 1$ h. The density of such obtained ceramic samples has been greater than 93.5% of X-ray theoretical density.

Dielectric permittivity ϵ and the tangent of dielectric losses $\tan\delta$ have been measured at frequency 1 kHz. Electromechanical properties have been investigated at room temperature. The phase composition and the parameters of elementary cell have been investigated by X-ray diffractometer.

3. Results and discussion

Dependencies $\epsilon(T)$ and $\tan\delta(T)$ for the CS samples are presented in Fig. 1. Fig. 2 shows $\epsilon_m(x)$, $T_m(x)$, $\chi(x)$

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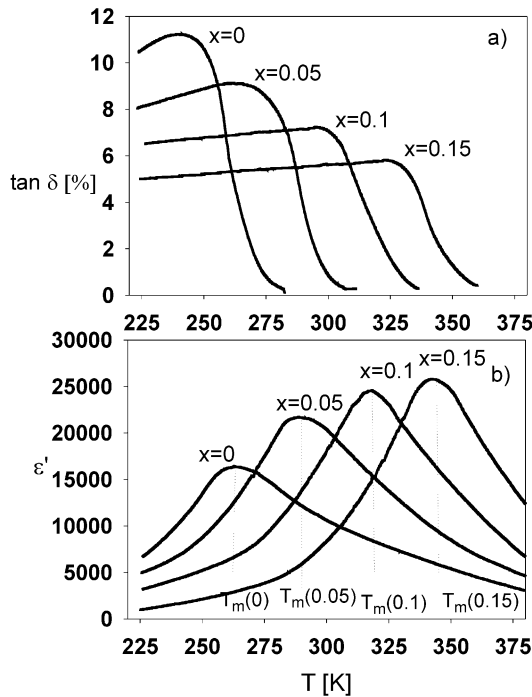


Fig. 1. The influence of the PbTiO₃ concentration (*x*) on the dependency of dielectric permittivity ϵ (b) and the tangent of losses $\tan\delta$ (a) on temperature for CS samples.

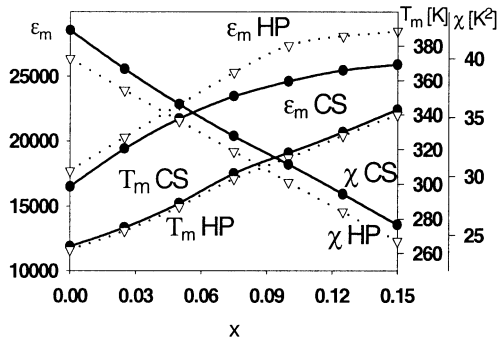


Fig. 2. The influence of the PbTiO₃ concentration (*x*) on the phase transition in (1-*x*)PbMg_{1/3}Nb_{2/3}O₃-(*x*)PbTiO₃, obtained by CS and HP methods. χ —degree of phase transition diffusion.

Table 1
Properties of (1-*x*)PMN-(*x*)PT ceramics—CS (1) and HP (2)

<i>x</i>	$\rho_{\text{exp}}^a / \rho_{\text{X-ray}}^b$ (%)		T_m (K)		ϵ_m ($T = T_m$)		χ^c (K ²)		a_0^d (nm) ($T = T_{\text{room}}$)	
	1	2	1	2	1	2	1	2	1	2
0	93.5	96.1	264	262	16470	17690	42.4	40.0	0.4048	0.4050
0.05	92.6	96.3	289	287	21720	22820	36.1	34.7	0.4044	0.4044
0.10	92.8	96.1	318	315	24600	27390	31.0	29.5	0.4040	0.4039
0.15	92.4	96.2	343	340	25900	28500	25.9	24.5	0.4036	0.4035

^a ρ_{exp} —Experimental density.

^b $\rho_{\text{X-ray}}$ —X-ray density.

^c χ —The degree of phase transition diffusion.

^d a_0 —Mean parameter of elementary cell at room temperature.

for PMN-PT obtained by both methods (CS and HP). It is seen from these figures that with increasing *x* $\epsilon(233\text{ K})$ decreases and ϵ_m increases. Higher values $\epsilon_m(T_m)$ for HP samples are related with higher values of density (see Table 1). The shift of T_m towards higher temperatures is similar for both CS and HP methods (i.e. the method does not substantially influence the value of T_m). The degree of the phase transition diffusion (χ in Table 1 and Fig. 2) decreases with increasing *x*. χ was estimated as in⁸ by fitting relative dielectric permittivity ϵ at $T > T_m$ to formula:

$$\epsilon^{-1}(T) = \frac{1}{\epsilon_m} + \frac{(T - T_m)^2}{2\epsilon_m\chi}, \quad (1)$$

where χ —the degree of diffusion of the phase transition (K²).

$\tan\delta(T)$ also reaches the maximum but at a temperatures smaller than T_m (Fig. 1a) what is characteristic for ferroelectrics with diffused phase transition. The maximum of $\tan\delta(T)$ and its value at 293 K decreases with increasing *x*. For $x = 0; 0.025$ and 0.05 $T_m < 293\text{ K}$. Such samples do not exhibit the hysteresis of relative strain vs. electric field $\eta(E)$ (Fig. 3 and Table 2). It means that at room temperature electrostriction is a

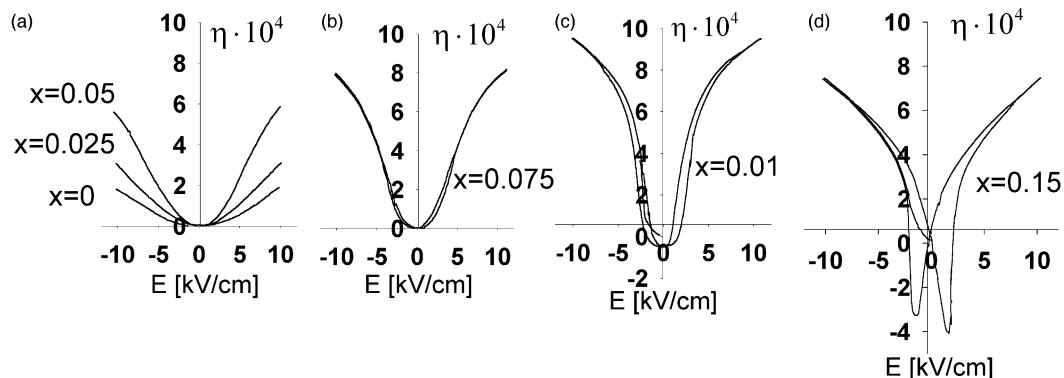


Fig. 3. The dependency of relative deformation (η) for ceramic samples (1-*x*) PMN-(*x*)PT on the electric field (*E*) and concentration of PbTiO₃(*x*).

Table 2
Electromechanical parameters (1-x)PMN-(x)PT ceramics—CS (1) and HP (2)

	CS		HP	
	$M_{11} \cdot 10^{16}$ (m ² /V ²)	H (%)	$M_{11} \cdot 10^{16}$ (m ² /V ²)	H (%)
0	2.0	0	1.6	0
0.05	8.1	0	8.0	0
0.075	18.1	5	20.0	6
0.10	22.4	15	24.2	16

main mechanism in such samples, which can be described (using scalar notation) by equation:

$$\eta = ME^2, \quad (2)$$

where:

$\eta = \Delta l/l_0$ —relative increase of the length of the sample (strain); M = electrostriction coefficients.

For $x \geq 0.075$ T_m is higher than room temperature. As a consequence at room temperature piezoelectric effect also gives its contribution into electromechanical deformation. The contribution of piezoeffect for $x \geq 0.075$ is confirmed by the hysteresis (H) of $\eta(E)$ (Fig. 3b–d). The value of H increases with increasing x (Fig. 3 and Tables 2–4).

Coefficients of electrostriction M_{11} for longitudinal deformation have been calculated on the basis of Eq. (2) from initial parts of $\eta(E)$ dependencies (Fig. 3) (i.e. for fields smaller than critical field that decreases with increasing x).

It is seen from results presented above that properties attributed in^{13–15} to 0.9PMN–0.1PT show 0.925PMN–0.075PT. To explain this fact two mixtures of oxides (PbO + TiO₂ + MgO + Nb₂O₅) have been prepared. The first mixture is stoichiometric while the second one has

Table 3
Parameters of 0.9PMN–0.1PT ceramics—sintered from oxides (MgO + Nb₂O₅ + PbO + TO₂) in conditions described in¹⁴

Stoichiometry	x (%)	T_m (K)	ϵ_m	$M_{11} \cdot 10^{16}$ (m ² /V ²)	H (%)
Stoichiometric	0.10	309	18380	10.5	10
1% excess PbO	0.10	311	22830	18.4	7

Table 4
The influence of MgO excess on dielectric and electrostrictive parameters of (1-x) PMN-(x)PT—method CS

MgO excess	$x = 0$			$x = 0.065$			$x = 0.075$		
	0%	2%	5%	0%	2%	5%	0%	2%	5%
T_m (K)	264	264	266	299	302	300	306	306	307
ϵ_m	16470	17000	15700	23380	17814	17800	23440	17600	17850
$M_{11} \cdot 10^{16}$ (m ² /V ²)	2.0	2.0	1.7	13.3	9.9	9.20	18.1	15.8	16.7
H (%)	0	0	0	2	2	2	5	7	8

1% (weight) excess of PbO. Then these two mixtures were used to prepare ceramics with technology described in.¹² X-ray analysis has shown that in the samples obtained from first mixture (stoichiometric) after sintering at $T_s = 1533$ K during $t_s = 1$ h the concentration of pyrochlore phase was equal to 1–2% what can lead to decrease of ϵ_m . The addition of excess 1% PbO allow to finish the synthesis. The main parameters of such obtained two series of the samples are presented in the Table 3.

Comparing the parameters of 0.9PMN–0.1PT obtained on the base of columbite (Table 1) and from simple oxides (Table 3) it is seen that in the second case T_m and ϵ_m are smaller. It stays in agreement with results of Swartz¹⁶ (who stated that in PMN–PT nonstoichiometry leads to a decrease of T_m what can be a result of Pb evaporation). The excess of PbO can compensate the deficit of Pb.

So, probably in works^{11,12} were presented the results of investigations of nonstoichiometric samples. If the deficit of Pb is small T_m does not decrease below the room temperature and in room temperature we can observe electromechanical hysteresis (see Table 3).

In some papers (for example¹⁶) it has been stated that a little excess of MgO makes the synthesis of Mg_{1+y}Nb₂O_{6+y} easier which improves dielectric and electro-mechanical parameters (for example increases ϵ_m). But our investigations similar to the results of⁷ do not confirm this conclusion. On the contrary, we think that the amount of MgO makes the process of sintering more difficult and samples have worse properties (see Table 4).

4. Conclusions

The main conclusions from this study are the following:

- HP samples possess higher density and better dielectric and electromechanical properties. It is typical especially for lead-containing perovskites. Lower temperature of sintering and shorter time prevents lead deficit.
- An excess PbO present in CS samples improves their properties. In many earlier studies the samples were probably nonstoichiometric as a result of the lead deficit. Experimental results obtained for such samples are different.

- Taking the above into account we have stated that properties attributed earlier to 0.9PMN–0.1PT possess ceramics 0.925PMN–0.075PT.
- The excess of MgO does not improve the properties of the samples. On the contrary such addition makes them worse.

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