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Preparation and Electrical Properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Solid Solutions

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Abstract—Ceramic samples of lead magnesium niobate (PMN) and $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT) solid solutions with $x = 0$, 0.05, 0.10, and 0.30 have been prepared by solid-state reactions, and their structural, electrical, and piezoelectric properties have been studied using x-ray diffraction, Rietveld profile analysis, impedance spectroscopy, and the resonance/antiresonance method. The results indicate that the use of nonstoichiometric columbite niobates enables the synthesis of phase-pure PMN and PMN–PT.

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INTRODUCTION

As shown in the 1980s [1], single crystals of $Pb[Zn_{1/3}Nb_{2/3}]_{1-x}Ti_xO_3$, which can also be represented in the form $(1 - x)PbZn_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ ($(1 - x)$PZN–xPT), offer extremely high piezoelectric activity in the [001] direction, even though their polar axis is [111]. Later, similar behavior was found in single crystals of $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$, which can be represented in the form $(1 - x)PbMg_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ ($(1 - x)$PMN–xPT) [2]. These materials possess high piezoelectric charge sensitivity ($d_{33} > 2500$ pC/N), a large electromechanical coupling coefficient ($k_{33} > 94\%$), and small hysteresis, with a strain within 1.7% [3]. In practice, however, bulk piezoelectric materials are typically utilized in polycrystalline form (ceramics). Studies of polycrystalline $(1 - x)Pb[Mg_{1/3}Nb_{2/3}]O_3$–$xPbTiO_3$ materials show that, for $x \le 0.075$, the electrostriction mechanism prevails; for $x > 0.075$, a major contribution to the electromechanical strain comes from the piezoelectric effect [4]. The chief drawback to polycrystalline materials in the systems in question is that they have low piezoelectric performance compared to their single-crystal analogs. Experimental data on the electrical properties of polycrystalline piezoelectric materials are often contradictory [5, 6]. Polycrystalline $PbMg_{1/3}Nb_{2/3}O_3$, $PbMg_{1/3}Nb_{2/3}O_3$–$PbTiO_3$, and $PbZn_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ often contain a pyrochlore phase, which has an adverse effect on their piezoelectric performance [7]. Different means are used to prevent pyrochlore formation. For example, in preparing $PbMg_{1/3}Nb_{2/3}O_3$, use is made of presynthesized $MgNb_2O_6$ (Swartz–Shrout method [7]), which reacts with appropriate amounts of Pb-containing components. To prevent the formation of a pyrochlore phase in the synthesis of $(1 - x)$PMN–xPT materials, Noheda et al. [8] added 15.5 wt % MgO and 2 wt % PbO in excess of the reaction stoichiometry. However, as shown by Ananta et al. [9], $MgNb_2O_6$ is unstable in a wide temperature range. Accordingly, neither preliminary $MgNb_2O_6$ synthesis [7] nor the addition of excess MgO and PbO [8] in the syntheses of polycrystalline $(1 - x)$PMN–xPT materials is capable of fully preventing the formation of a pyrochlore phase and the associated degradation of their electrical (piezoelectric) performance. Among other precursors for the synthesis of $(1 - x)$PMN–xPT are $PbNb_2O_6$ [10] and $Pb_3Nb_2O_8$ [11, 12]. Such approaches, however, also do not always insure the preparation of single-phase ceramics. Saborsky et al. [13] and Singh and Pandey [14] obtained $(1 - x)$PMN–xPT materials with relative densities of up to 98% using various lead and magnesium salts as starting reagents. Their materials, however, had rather low piezoelectric performance [10].

Recent work [15] has shown that slight deviations from stoichiometry have a significant effect on the structure and properties of $MgNb_2O_6$ (columbite structure), which can be used as a starting material in the synthesis of $(1 - x)$PMN–xPT solid solutions. In particular, nonstoichiometric $MgNb_2O_6$ has been shown to possess a higher microwave quality factor in comparison with the stoichiometric material.

The purpose of this work was to investigate the formation of $(1 - x)$PMN–xPT ($x = 0$, 0.05, 0.10, 0.30) solid solutions, with a nonstoichiometric columbite niobate as a starting material, and to study their structural and electrical properties.

EXPERIMENTAL

The starting chemicals used were extrapure-grade Nb_2O_5, reagent-grade MgO, pure-grade PbO, analytical-grade $PbCO_3$, reagent-grade $PbTiO_3$, and extrapure-grade TiO_2. $Mg_{1+y}Nb_2O_6$ ($y = 0, 0.01, 0.03$) niobates were synthesized by reacting appropriate ratios of dried MgO and Nb_2O_5. The starting mixtures were prepared and homogenized by grinding with bidistilled water in a vibratory ball mill, using corundum grinding media. Next, the mixtures were dried, screened through a nylon-6 sieve, and fired at 1140°C for 6 h. Lead metaniobate, $PbNb_2O_6$ (changbaiite), was prepared by reacting a stoichiometric mixture of PbO and Nb_2O_5 at 850°C for 4 h.

$(1-x)$PMN–xPT solid solutions were synthesized through firing at temperatures from 700 to 850°C for 4–6 h. After firing and homogenization, a binder was added to the powder, which was then pressed into disks 10–14 mm in diameter and 3–4 mm in thickness. The compacts, packed with Pb-containing material, were sintered at temperatures from 1150 to 1250°C.

X-ray diffraction (XRD) measurements were performed on a DRON-4-07 powder diffractometer (CuK_α radiation). Structural parameters were determined by the Rietveld profile analysis method. XRD patterns were run in the angular range $2\theta = 10°–150°$ in a step-scan mode with a step size $\Delta 2\theta = 0.02°$ and a counting time of 10 s per data point. As external standards, we used SiO_2 (2θ calibration) and Al_2O_3 (intensity standard).

The complex impedance $Z = Z' + iZ''$ (where Z' and Z'' are the real and imaginary parts of the complex impedance) was measured in wide frequency (100 Hz to 1 MHz) and temperature (20–300°C) ranges using a Solartron Analytical 1260A impedance/gain-phase analyzer.

Electrical contacts were made by firing silver paste. The samples were poled in silicone oil at 120°C by a dc electric field of 10 kV/cm. Piezoelectric parameters (k_p, k_{31}, k_{33}, d_{31}, and d_{33}) were measured at room temperature by the resonance/antiresonance method, using two types of specimens: bars measuring 2 × 2 × 5 mm (in k_{33} and d_{33} measurements) and disks 13.5 mm in diameter and 1 mm in thickness (k_p, k_{31}, and d_{31} measurements).

RESULTS AND DISCUSSION

At slight deviations from stoichiometry, $0 < y \leq 0.03$, $Mg_{1+y}Nb_2O_6$ materials are single-phase and have the columbite structure [15]. The microwave quality factor, $Q = 1/\tan\delta$, in this y range is larger than that of the stoichiometric material ($y = 0$). One reason for the increased electrical Q in the range $0 < y \leq 0.03$ is the reduction in lattice strain, which has an advantageous effect on the electrical properties of the materials under consideration [16]. In view of this, we first synthesized $Mg_{1+y}Nb_2O_6$ niobates in the composition range ($y = 0$, 0.01, 0.03) where these materials are single-phase. Lead magnesium niobate was synthesized by reacting $Mg_{1+y}Nb_2O_6$ with different magnesium contents and PbO according to the scheme

$$Mg_{1+y}Nb_2O_6 + 3PbO \longrightarrow 3Pb(Mg_{(1+y)/3}Nb_{2/3})O_3. \quad (1)$$

The present results indicate that heat treatment in the range 750–800°C leads to the formation of the perovskite structure with a small amount of an impurity pyrochlore phase ($Pb_3Nb_4O_{13}$) (Fig. 1a).

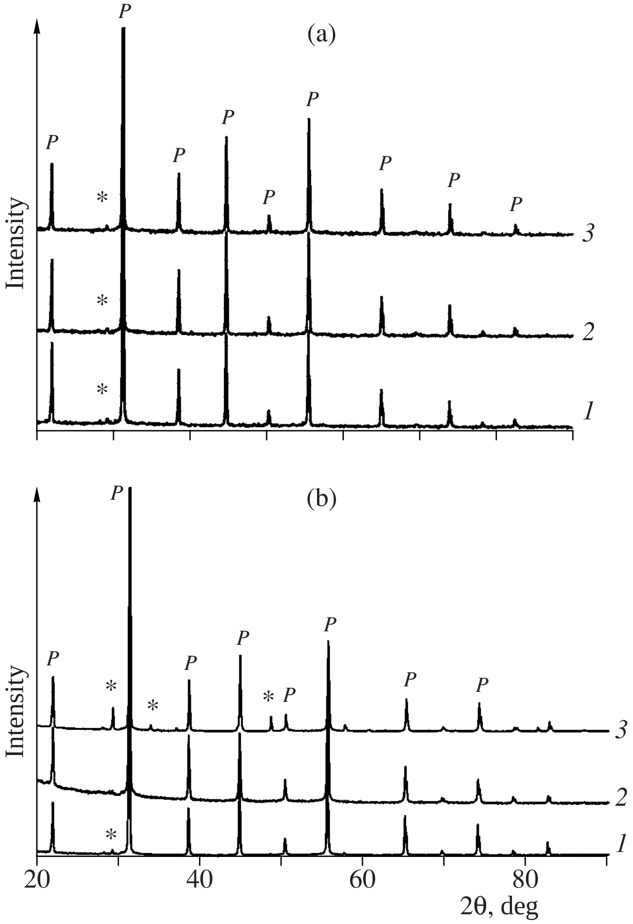

Fig. 1. (a) XRD patterns of powders for the preparation of the lead magnesium niobate $PbMg_{(1+y)/3}Nb_{2/3}O_3$ from a mixture of $Mg_{1+y}Nb_2O_6$ and PbO after heat treatment at 780°C for 4 h; (b) XRD patterns of the ceramics prepared by sintering the powders at 1200°C for 1 h. y = (*1*) 0, (*2*) 0.01, (*3*) 0.03. * = $Pb_3Nb_4O_{13}$ pyrochlore, $P = PbMg_{(1+y)/3}Nb_{2/3}O_3$ perovskite.

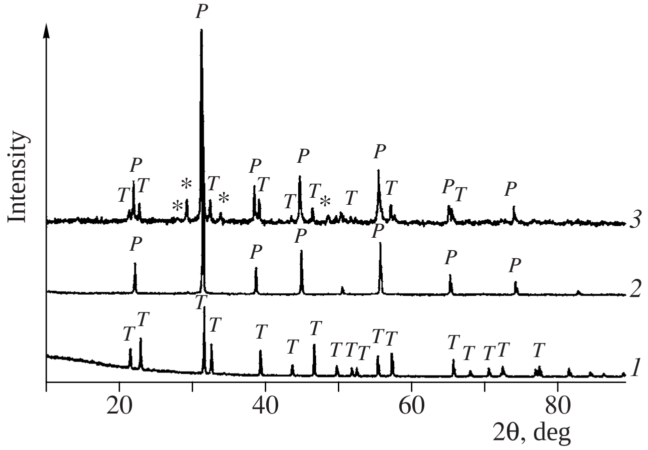

Fig. 2. XRD patterns of (*1*) $PbTiO_3$ and (*2*) $PbMg_{1.01/3}Nb_{2/3}O_3$ powders and (*3*) their mixture corresponding to the $0.7PbMg_{1.01/3}Nb_{2/3}O_3$–$0.3PbTiO_3$ solid solution after heat treatment at 820°C. *T* = tetragonal $PbTiO_3$ (macedonite), *P* = cubic $PbMg_{1.01/3}Nb_{2/3}O_3$ perovskite, * = $Pb_3Nb_4O_{13}$ pyrochlore.

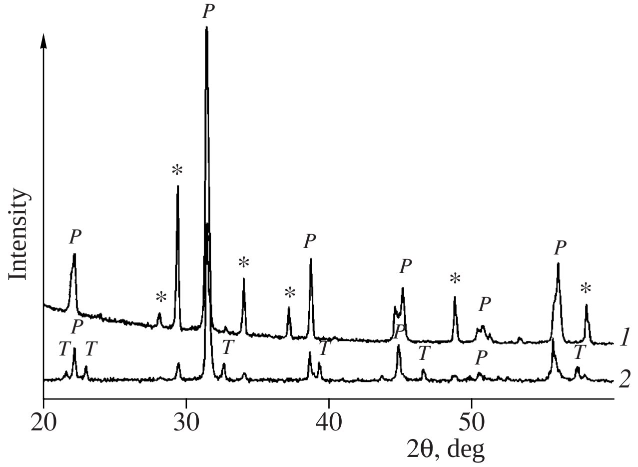

Fig. 3. XRD patterns of (*1*) the powder for the preparation of the $0.7PbMg_{1.01/3}Nb_{2/3}O_3$–$0.3PbTiO_3$ solid solution from a stoichiometric $PbNb_2O_6$ + PbO + MgO + TiO_2 mixture after heat treatment at 800°C for 4 h and (*2*) the ceramic prepared by sintering the powder at 1200°C for 1 h. * = $Pb_3Nb_4O_{13}$ pyrochlore, *T* = $PbTiO_3$, *P* = $PbMg_{1/3}Nb_{2/3}O_3$ perovskite.

$Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with relative densities from 94 to 98% were obtained by firing at 1180–1200°C for 1 h. The XRD data for the $PbMg_{1/3}Nb_{2/3}O_3$ ceramics (Fig. 1b) demonstrate that the ceramic prepared using $Mg_{1+y}Nb_2O_6$ with $y = 0.01$ is essentially free of the pyrochlore phase, whereas at $y = 0$ and, especially, at $y = 0.03$, the ceramics contain significant amounts of the pyrochlore phase (Fig. 1b). In connection with this, in subsequent syntheses of $(1 - x)$PMN–xPT solid solutions the $Mg_{1+y}Nb_2O_6$ columbite with $y = 0.01$ was used as a starting material.

$(1 - x)$PMN–xPT solid solutions were synthesized using different starting reagents. According to XRD data, no solid solutions were formed in the range 700–1100°C if lead titanate and presynthesized lead magnesium niobate were used as starting reagents (Fig. 2). Instead, we obtained a mixture of the starting reagents and $Pb_3Nb_4O_{13}$ pyrochlore.

Also, no $(1 - x)$PMN–xPT solid solutions were obtained by reacting appropriate amounts of $PbTiO_3$, $MgNb_2O_6$, and PbO or $PbNb_2O_6$, PbO, TiO_2, and MgO (Fig. 3).

At the same time, by reacting appropriate ratios of presynthesized $Mg_{1.01}Nb_2O_6$ (columbite structure), TiO_2, and PbO for 1 h, we obtained single-phase $(1 - x)$PMN–xPT solid solutions at temperatures as low as 720–800°C (Fig. 4). The sintering temperature of the $(1 - x)$PMN–xPT ceramics with x from 0 to 0.30 was 1140–1220°C and decreased with increasing x.

In structural studies, we determined the symmetry of the synthesized materials at room temperature. Pure

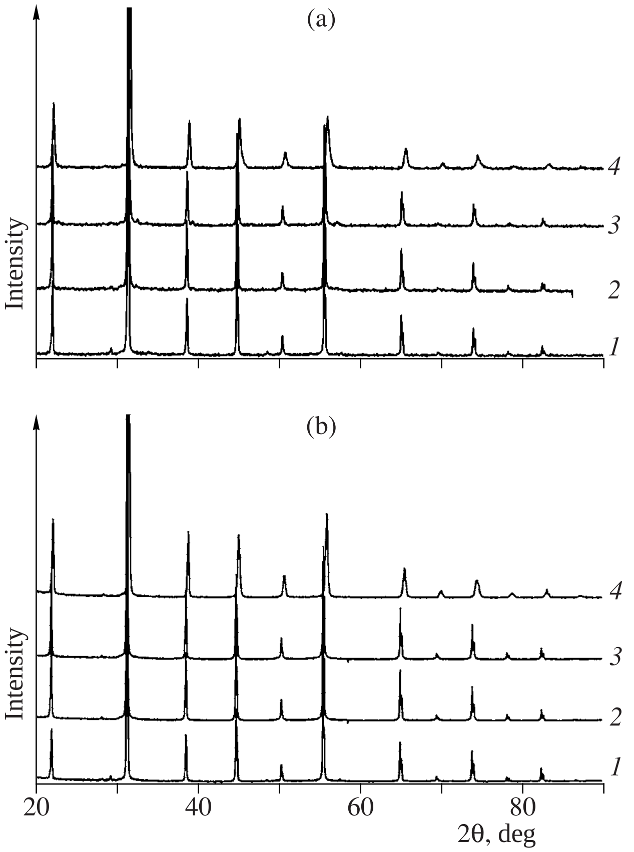

Fig. 4. XRD patterns of (a) $(1-x)PbMg_{1.01/3}Nb_{2/3}O_3$–$xPbTiO_3$ powders prepared by reacting $Mg_{1.01}Nb_2O_6$ + PbO + TiO_2 mixtures at 780°C for 4 h and (b) the ceramics prepared by sintering the powders at 1200°C for 1 h: x = (*1*) 0, (*2*) 0.05, (*3*) 0.10, (*4*) 0.30.

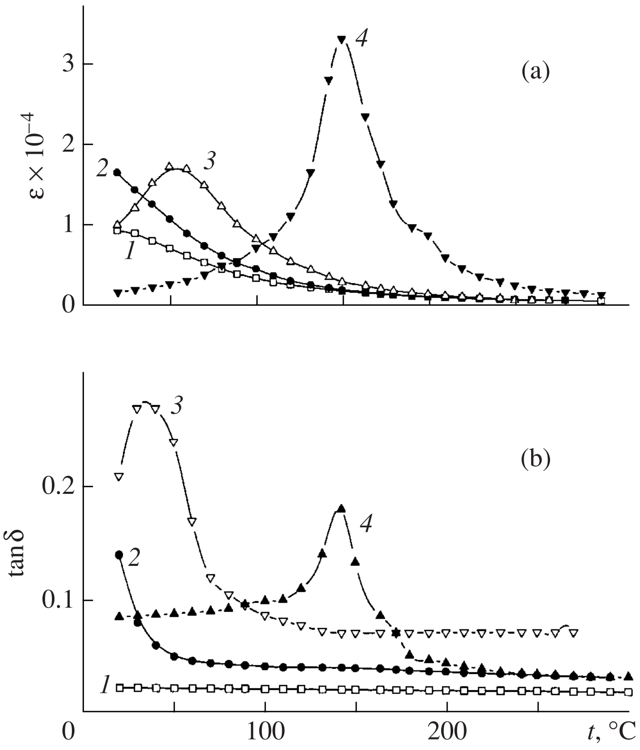

Fig. 5. Temperature dependences of (a) dielectric permittivity and (b) loss tangent at 50 kHz for $(1-x)PbMg_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ ceramics with x = (*1*) 0, (*2*) 0.05, (*3*) 0.10, and (*4*) 0.30.

PMN and $(1-x)$PMN–xPT with small x were reported by several researchers to have a cubic structure [17–19] because their Curie points are below room temperature. However, since these materials undergo a diffuse phase transition, they are not necessarily paraelectric at room temperature, and their symmetry may be lower. In particular, orthorhombic [20] and rhombohedral [21] symmetries were assumed. Such symmetries were thought to exist in separate microregions within the cubic matrix, rather than being macroscopic. Rhombohedral symmetry appears more likely because it is supported by experimental data for $(1-x)$PMN–xPT solid solutions containing 30 to 32.5% $PbTiO_3$ [22]. At lower PT contents, the symmetry remains unclear. Thomas et al. [21] were the first to show that space group $R3m$ best represents room-temperature neutron diffraction data for PMN.

It was, therefore, of interest to find out to what extent rhombohedral symmetry better represents the XRD data for the synthesized $(1-x)$PMN–xPT solid solutions at small x (0–0.1) in comparison with cubic symmetry. As a first approximation, we took two space groups which might represent the symmetry of the compounds in question: $Pm\bar{3}m$ (cubic symmetry) and $R3m$ (rhombohedral symmetry).

The table lists the lattice constants, positional parameters, and site occupancies in the $(1-x)$PMN–xPT ceramics with x = 0, 0.05, 0.10, and 0.30 under the assumption that they have a rhombohedral structure. At all of the x values, the Bragg R factor for cubic symmetry (sp. gr. $Pm\bar{3}m$) is a factor of 1.5–2 larger than that for rhombohedral symmetry (sp. gr. $R3m$). Thus, rhombohedral symmetry better represents our experimental data, suggesting that, at room temperature, the macroscopic symmetry of the $(1-x)$PMN–xPT solid solutions is rhombohedral.

Rhombohedral symmetry is also evidenced by the displacement of the O^{2-} ions. In particular, if the symmetry were cubic, the oxygen position coordinates in space group $R3m$ would be $x = 0.16667$ and $z = 0.3333$. It can be seen from the table, however, that the oxygens are notably displaced from this position (by more than several standard deviations) and that the displacement

Unit-cell parameters, positional parameters, and site occupancies in $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ceramics

x	0*	0	0.05	0.10	0.30	0.30**
Unit-cell parameters						
a, Å	5.7194(3)	5.7207(4)	5.7144(2)	5.7073(6)	5.6845(5)	5.6940(4)
c, Å	7.0101(7)	7.0050(9)	6.9992(5)	6.9880(9)	6.9595(4)	6.9601(8)
V, Å^3	198.59(3)	198.54(4)	197.93(2)	197.14(5)	194.76(3)	195.43(4)
Positional parameters						
Mg/Nb/Ti						
z	0.478(2)	0.492(2)	0.488(2)	0.484(4)	0.474(5)	0.479(5)
O						
x	0.158(6)	0.171(5)	0.184(2)	0.194(1)	0.214(3)	0.209(4)
z	0.348(5)	0.343(1)	0.348(6)	0.351(6)	0.357(5)	0.353(6)
Site occupancies						
Mg	0.333	0.333	0.317	0.303	0.256	0.256
Nb	0.667	0.667	0.635	0.606	0.513	0.513
Ti	0.000	0.000	0.048	0.091	0.231	0.231
Pb	0.940(5)	0.928(3)	0.931(4)	0.940(4)	0.950(9)	0.99(3)
O	1.000	1.000	1.000	1.000	1.000	1.000
Agreement factors						
R_B, %	5.34	7.70	4.45	4.96	5.07	7.5
R_f, %	4.65	5.37	4.43	4.19	4.55	7.8
Ferroelectric displacement						
$\delta_{Pb–O}$, Å	0.103	0.068	0.103	0.123	0.165	0.137
$\delta_{Mg/Nb/Ti–O}$, Å	0.257	0.124	0.187	0.235	0.346	0.283

Notes: $R3m$ structure: Pb in position $3a$ $(0\ 0\ z)$ with $z_{Pb} = 0$, Mg/Nb/Ti in $3a$ $(0\ 0\ z)$, and O in $9b$ $(x\ {-x}\ z)$.
Ferroelectric displacement is the displacement of the cation from the center position in its oxygen octahedron.
* Single crystal.
** Hot-pressed material.

increases with $PbTiO_3$ content. This attests to distortion of the oxygen octahedron, which is atypical of cubic symmetry. Yet another indication of rhombohedral symmetry is the displacement of the Mg, Nb, and Ti ions (which occupy the same crystallographic site) from the $z = 0.5$ characteristic of cubic symmetry by several standard deviations, which also increases with $PbTiO_3$ content. As x increases from 0 to 0.3, the lattice constants decrease systematically, and the atomic position coordinates vary linearly. Over the entire composition range studied ($x = 0.1$–0.3), the lattice constants follow Vegard's law, which also suggests that, at small x, the space group of the $(1 - x)$PMN–xPT solid solutions is $R3m$.

The Rietveld analysis results also indicate that the Pb site occupancy rises with x. This may be interpreted as evidence that Pb losses decrease with decreasing sintering temperature. Analysis of the cation displacement from the center position in the oxygen octahedra (ferroelectric displacement) in conjunction with earlier results [23] leads us to conclude that, with increasing x, the [111] polarization decreases.

The temperature dependences of dielectric permittivity ε and loss tangent $\tan\delta$ for the synthesized $(1 - x)$PMN–xPT materials (Fig. 5) agree with earlier results. The 0.7PMN–0.3PT ceramic was found to possess high piezoelectric performance: $k_p = 0.54$, $k_{31} = 0.32$, $k_{33} = 0.65$, $d_{31} = 196$ pC/N, and $d_{33} = 600$ pC/N.

CONCLUSIONS

The present results indicate that the use of the nonstoichiometric columbite niobate $Mg_{1+y}Nb_2O_6$ enables the synthesis of phase-pure$(1 - x)$PMN–xPT solid solutions.

Over the entire composition range studied, $x = 0$–0.30, the space group of the $(1 - x)$PMN–xPT solid solutions is $R3m$.

The ceramics prepared in this study offer high piezoelectric performance.

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