MICROSTRUCTURE AND ELECTRICAL RESPONSE OF $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ RELAXOR CERAMICS

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Ceramic samples of a solid solution of 10 mol.% lead titanate $PbTiO_3$ (PT) in lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) were investigated from the view-point of phase transition behavior and electrical properties. Dielectric spectroscopy in a frequency region of 10^2 - 10^6 Hz was carried out to study the temperature and frequency dependence of the weak-field dielectric response in 0.9PMN-0.1PT material prepared via a columbite precursor route. The temperature T_m of the observed maxima in the dielectric permittivity (ε_m) was found to shift from 45.4 to 58.5°C and ε_m decreased from 4500 to 4060 as the frequency increased from 100 Hz to 1 MHz. The characteristics of a diffuse phase transition (DPT) behavior ($\gamma \approx 1.8$ and $\delta_\gamma \approx 30$°C) were determined using an extended Curie-Weiss law. The relaxor features of ferroelectrics were also demonstrated by a "slim" ferroelectric hysteresis loop. Non-zero values of the piezoelectric parameters ($k_p \approx 1.6$ %, $d_{31} \approx -3.6$ pC/N) and spontaneous polarization ($P_s \approx 2.4$ μC/cm²) were observed at 80°C, indicating the existence of nanopolar regions in the structure far above the T_m.

INTRODUCTION

Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) belongs to a technologically important class of complex $Pb(B' B'')O_3$ perovskite materials known as relaxor ferroelectrics. They are characterized by an anomalously high dielectric permittivity and broad, frequency-dependent maxima in the real and imaginary parts of the complex dielectric permittivity [1]. The phase transitions in these materials are called as the diffuse phase transition.

Among a number of electrostrictive ferroelectrics, that have been obtained on the basis of complex lead niobates of $Pb(B' B'')O_3$-type, the solid solutions of relaxor PMN and normal ferroelectric $PbTiO_3$ have been the most studied systems for the last ten years because of very interesting combination of large electrostrictive strains and a minimal or negligible hysteresis in the strain-field dependence [2,3]. Moreover, remarkably large piezoelectric constants and a huge dielectric permittivity were reported for some compositions of PMN-PT pseudo-binary system [4,5]. In recent years, a lot of fundamental and practical investigations have been carried out for the composition of 0.9PMN-0.1PT that is considered as an attractive material for numerous applications such as high-resolution sonar devices and ultrasonic transducers for medical diagnostic systems, small size multi-layer ceramic capacitors and high-strain electrostrictive actuators because of its large dielectric response and electrostriction [6].

All superior and useful properties of relaxor ferroelectrics have their origin in the strange polarization mechanism that is associated with the relaxor-type DPT. Despite the extensive fundamental research of PMN-related materials the universal mechanisms governing the phase transition and relaxation are still not clearly understood [7,8,9]. Microscopically, it is generally accepted that the relaxor ferroelectric properties of lead-based complex perovskites are very closely related to their B-site cation arrangement. In PMN it does appear that a structure contains Mg^{2+}-rich ordered nanosized domains (nonstoichiometrically 1:1-ordered regions with a short coherence length of 2-50 nm) dispersed in a Nb^{5+}-rich disordered matrix [10].

Traditional solid-state reaction synthesis of this kind of compounds has been found always to result in the formation of a non-ferroelectric pyrochlore phase of low permittivity. The presence of such secondary phase significantly degrades the final electrical properties of relaxors. The problems associated with pyrochlore formation during ceramic processing can be effectively eliminated, for example, via the columbite precursor method as suggested by Swartz and Shrout [11].

As the excellent dielectric and electromechanical properties of PMN-based ferroelectrics are produced by a large electrostriction existing just in a relaxor phase and the relaxor compositions of the pseudo-binary PMN-PT system are reported for PT contents less than 30 mol.% [7,12], the purpose of the present work is to

characterize the room-temperature ferroelectric state and phase transition behavior of 0.9PMN-0.1PT ceramics prepared by the columbite method. The resulting dielectric and piezoelectric properties are also discussed in terms of structure-property relationships.

EXPERIMENTAL

The $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ ceramic samples (abbreviated as PMNT/10 hereafter) that were used for this study were prepared using conventional oxide mixing via a columbite precursor method. More details of the syntheses of columbite $MgNb_2O_6$ precursor powder can be found in reference [11]. The mixture of considered amounts of Pb_3O_4, TiO_2 and $MgNb_2O_6$ oxide powders was ball-milled, dried and then calcined at 850°C for 2 h in alumina crucible. After that, the reacted material was additionally ball-milled to ensure a fine particle size before sintering. The dried powder was axially pressed into disks of 13 mm in diameter and about 2 mm in thickness. The green pellets were sintered for 2 hours at 1200°C on a Pt plate. The apparent density of the sintered ceramics was determined by water immersion using the Archimedes method. The phase structure was detected for flat disks on X-ray diffractometer (Philips, model X'Pert Pro) using CuK_α radiation. The scanning rate was 4°/min over the angular range of $20° \leq 2\Theta \leq 80°$ with incremental step of 0.015°. The lattice parameters were calculated based on the least-square method (LAPOD program) with over six peaks of diffraction pattern. The volume percentage of perovskite phase present in the material was calculated using the following equation [11]:

$$\% \text{ perovskite} = \frac{(I_{110})_{perov}}{(I_{110})_{perov} + (I_{222})_{pyro}} \; 100 \qquad (1)$$

where (I_{110}) and (I_{222}) are the major X-ray peak intensities for a perovskite phase and a pyrochlore phase, respectively.

Scanning electron micrographs (SEM, Tesla BM 340) were taken from polished and chemically etched sections of the ceramic surfaces for grain size and morphology determination. For the property measurement, the sintered disks were lapped step-by step with SiC papers to approximately 0.2 mm thickness, and then cleaned with methanol using an ultrasonic cleaner. The major faces of specimens were electroded by applying Ag paste, and fired at 830°C for 30 min. The poling process was carried out in a silicone oil bath at a temperature of 110°C by applying a DC field of 30 kV/cm on the sample.

Weak-field low-frequency dielectric measurements were carried out on an automated system, whereby an impedance analyzer (Hewlett-Packard, model HP 4192A) was controlled by a computer. Temperature dependencies of the relative dielectric permittivity, as calculated from the capacitance of the sample and its geometry, and dissipation factor were measured continuously on heating at various frequencies in range of 100 Hz - 1 MHz. The samples were placed in a small furnace, which can be operated at a temperature range from room temperature to 500°C. The temperature inside of furnace was measured using a voltage meter (Keithley, model 177 Microvolt DMM meter) with a chromel-alumel thermocouple placed near the surface of the sample and controlled to within ± 1°C using a purpose-made temperature controller. Heating runs were performed at the rate of 5°C/min outside of phase transition region and around the temperature of dielectric permittivity maximum with the rate of 0.5°C/min.

The dielectric permittivity of relaxor ferroelectrics near the Curie region ($T \geq T_m$) is governed by a modified Curie-Weiss law. Martirena and Burfoot [13] proposed a power relation to describe the temperature dependence of the relative dielectric permittivity in a paraelectric phase as follows:

$$\frac{1}{\varepsilon_r(\omega, T)} = \frac{1}{\varepsilon_m(\omega)} \left[1 + \frac{[T - T_m(\omega)]^\gamma}{2\delta_\gamma^2}\right], \qquad (2)$$

where ω is the angular frequency, T_m is the temperature at maximum dielectric permittivity ε_m, and δ_γ and γ are the diffuseness parameter and critical exponent, respectively.

The value of γ ($1 \leq \gamma \leq 2$) is the expression of the degree of dielectric relaxation in a relaxor. When $\gamma = 1$, equation 2 express the Curie-Weiss behavior of the ferroelectrics, while for $\gamma = 2$, equation 2 is identical to a quadratic Smolensky's relation [14].

After 24 h aging at room temperature, complex impedance characterization was carried out with the above mentioned impedance analyzer by an iterative resonance-antiresonance method proposed by Alemany et al. [15]. The temperature dependence of the spontaneous ferroelectric polarization was measured on cooling over the temperature range of 20-300°C. Thermally stimulated electric current was accumulated and the total charge was registered as a function of tempe-rature with a programmable electrometer (Keithley, model 6512). The ferroelectric hysteresis (P-E) loops were characterized by using a computer controlled virtual ground circuit with a purpose-made integrator. The cycling frequency was 0.01 Hz and the maximum switching field applied on the sample was 1000 V.

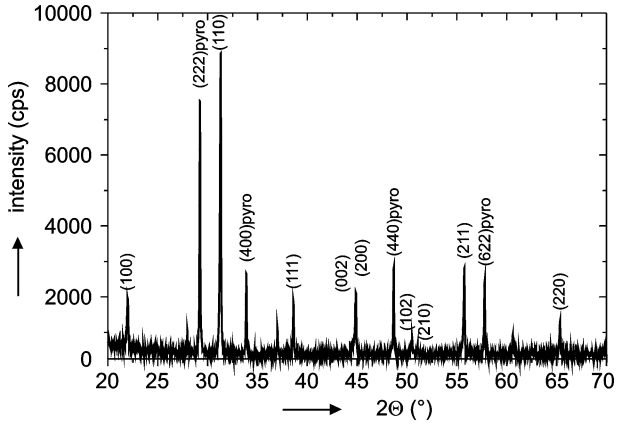

Figure 1. Room-temperature X-ray diffraction pattern for 0.9PMN-0.1PT ceramics.

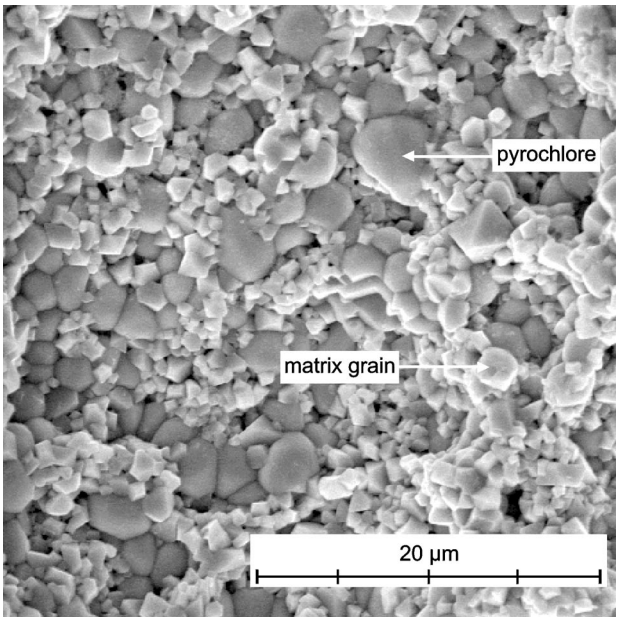

Figure 2. SEM micrograph of 0.9PMN-0.1PT ceramics sintered at 1200°C for 2 h.

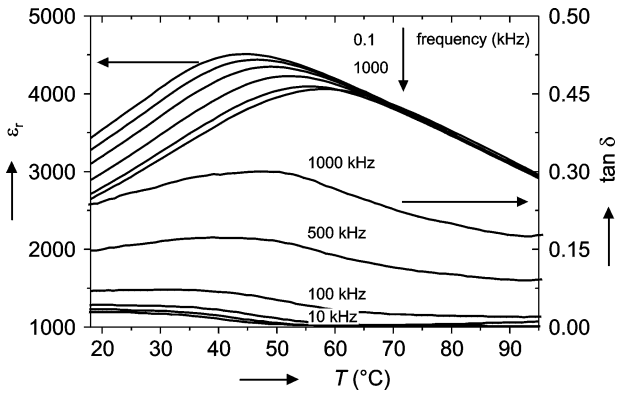

Figure 3. Temperature dependencies of the relative dielectric permittivity and dissipation factor of 0.9PMN-0.1PT ceramics measured at 0.1, 1, 10, 100, 500 and 1000 kHz.

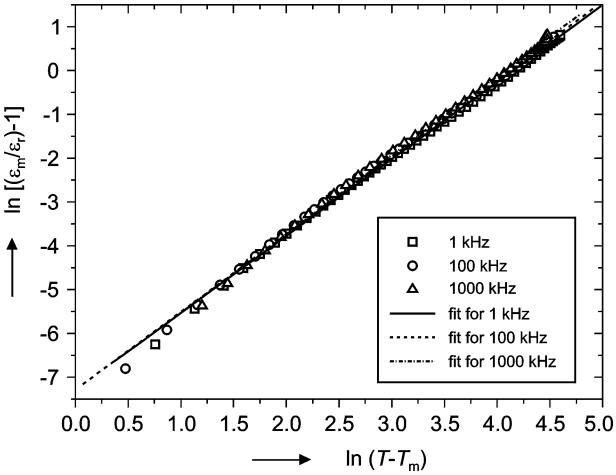

Figure 4. Plot of $\ln[(\varepsilon_m/\varepsilon_r)-1]$ against $\ln(T-T_m)$ for 0.9PMN-0.1PT ceramics at 1, 100 and 1000 kHz. T_m and ε_m are the experimental results, solid and dashed lines are fits obtained from equation 2.

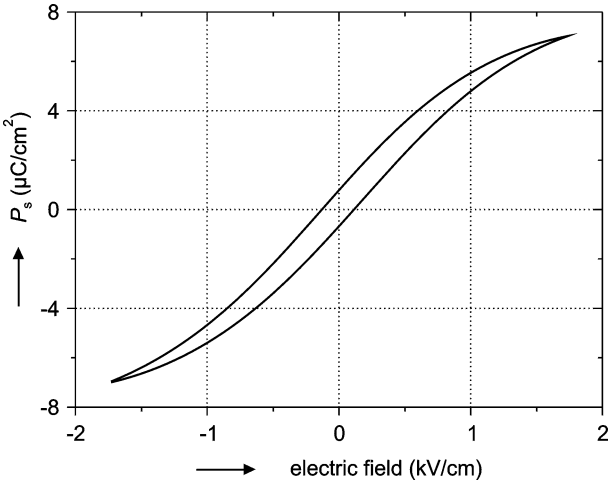

Figure 5. Dielectric hysteresis loop for 0.9PMN-0.1PT measured at 25°C.

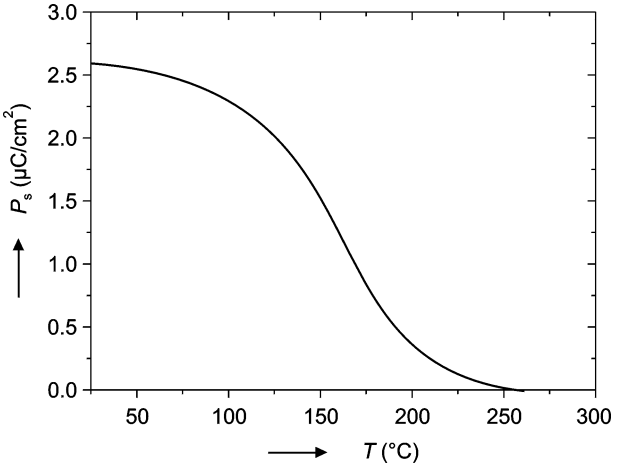

Figure 6. Temperature dependence of the spontaneous ferroelectric polarization for 0.9PMN-0.1PT ceramics.

Table 1. Dielectric parameters of 0.9PMN-0.1PT involved in an extended Curie-Weiss model.

sample	frequency $\times 10^3$ (Hz)	T_m (°C)	ε_m	γ	δ_γ (°C)
0.9PMN -	0.1	45.38	4509	1.60	22.0
0.1PT	1	46.63	4438	1.72	27.2
	10	48.97	4348	1.74	27.5
	50	51.22	4269	1.74	27.5
	100	52.34	4227	1.74	27.7
	200	53.43	4177	1.75	27.5
	500	55.49	4093	1.81	30.2
	1000	58.45	4064	1.82	30.4

T_m - temperature of dielectric permittivity maximum (ε_m), γ - critical exponent, δ_γ - diffuseness parameter.

RESULTS AND DISCUSSIONS

Ceramic properties

Figure 1 shows the X-ray diffraction (XRD) pattern of PMNT/10 obtained at room temperature. From the figure, it is apparent that the sample exhibits a pseudo-cubic perovskite structure (lattice parameter a_c = 0.403 nm) with large amounts of a secondary phase. X-ray peak intensities of the pyrochlore phase are considerable in XRD pattern, although the columbite method was used in preparation process. The volume fraction of a perovskite phase is lower than 75 %, and thus one can correlate the decrease in the bulk density (ρ < 95 % of theoretical density) with the decomposition of perovskite phase during sintering process into Mg-rich pyrochlore phase and volatile PbO. The SEM micrograph, as shown in figure 2, reveals the presence of secondary pyrochlore phase in the structure of PMNT/10. Cubic particles (≈ 2.5-3 μm) were found to surround the matrix grains with size of 1 μm.

Electrical properties

The temperature dependence of the relative dielectric permittivity (ε_r) and dissipation factor (tan δ) for the 0.9PMN-0.1PT ceramic samples is plotted in figure 3 at six different frequencies. As the measuring frequency increases the dielectric permittivity maximum (ε_m) decreases and its temperature (T_m) moves towards higher temperature. The dielectric dispersion that occurs at temperatures slightly above the maximum permittivity temperature persists down to room temperature. Therefore, it should be noted that no dielectric anomaly corresponding to a spontaneous macroscopic (zero-field) transformation toward a long-range ordered ferroelectric state has been observed on the low-temperature side of $\varepsilon_r(T)$ peak up to room temperature. The loss tangent shows only very small decrease with decreasing temperature below the T_m and its value is much higher than that above the temperature of dielectric permittivity maximum. A strongly diffuse dielectric peak, and the above mentioned dielectric response behavior, are characteristic of ferroelectric relaxors with a partially disordered perovskite structure. The room temperature state of PMNT/10 may be considered a typical relaxor state with a dynamic polar region on a nanometric scale.

Considering an extended Curie-Weiss law (equation 2) for our PMNT/10 sample, the graph of $\ln[(\varepsilon_m/\varepsilon_r)-1]$ plotted against $\ln(T-T_m)$ provided the value of the critical exponent (γ) and $\ln(2\delta_\gamma^2)$ as a slope and y-axis intercept, respectively. The fits obtained from equation 2 for 1, 100 and 1000 Hz are shown as representative in figure 4. The calculated dielectric parameters are given together with the values of T_m and ε_m in table 1. Since the Curie-Weiss behavior can be considered as a signature of the onset of long-range order, the deviation from the Curie-Weiss law in PMNT/10 sample indicates the decrease of the long-range ferroelectric correlation. The rise in broadening of dielectric peak (δ_γ) and the increasing of critical exponent (γ) with an increase in frequency suggest that the broadening effect on the phase transition is more pronounced at higher frequencies.

The field-dependent hysteresis behavior, as another manifestation of the relaxor behavior of PMNT/10, is given in figure 5. A "slim" hysteresis loop (the remanent polarization P_r = 0.7 μC/cm^2, the coercive field E_c = 3.8 kV/cm) is typical of a phase with a suppressed long-range ferroelectric interaction between dipoles. The absence of a micron-sized ferroelectric domain state [7] resulted in only a slight ferroelectricity of the sample at room temperature.

Figure 6 presents the behavior of the spontaneous polarization (P_s) as a function of temperature for PMNT/10 ceramics. The character of the phase transition as expected and deduced from dielectric measurements is of the diffuse type. We note, that the polarization was found to be non-zero till 270°C, indicating the

presence of local dipole moments (RMS polarization) at temperatures far above T_m (≈ 45°C).

An impedance spectroscopy performed on PMNT/ /10 at various temperatures also suggests the existence of polar micro regions well above the T_m. Due to the thermal evolution of ferroelectric polarization, piezoelectric parameters such as a planar coupling factor (k^p) and a piezoelectric d_{31} coefficient decrease with increasing temperature up to the paraelectric phase, but they remain non-zero at 80°C (k_p = 1.59 %, d_{33} = -3.6 pC/N).

CONCLUSION

The structural, dielectric, pyroelectric, ferroelectric and piezoelectric properties of 0.9PMN-0.1PT solid solution systems were investigated in order to characterize a ferroelectric state of the ceramic material widely employed, nowadays, for sensor and actuator applications. The experimental data obtained in this work allowed us to conclude results as follows.

The columbite precursor method that was adopted in preparation process resulted in a perovskite structure with a large amount of secondary pyrochlore phase (≈ 25 vol.%). The crystal symmetry of 0.9PMN-0.1PT at room temperature is pseudocubic with a lattice parameter a_c equals to 0.403 nm. The sample exhibits a DPT relaxor behavior around the dielectric permittivity maximum, characterized by a strongly diffuse dielectric peak and a shift of the dielectric permittivity maximum to a higher temperature with increasing measurement frequency. The critical exponent (γ) and broadening parameter (δ_γ), as calculated from a modified Curie-Weiss law, were found to be close of the values reported for the relaxor ferroelectrics, and in conjunction with their frequency dependency the results demonstrate a dynamic disorder in material. From the pyroelectric, ferroelectric and piezoelectric measurements, it was revealed that the micro-polar regions, which are considered to be responsible in a large extent for unusual relaxor characteristics exist in 0.9PMN-0.1PT far above the critical region ($T >> T_m$).

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MIKROŠTRUKTÚRA A ELEKTRICKÁ ODOZVA $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ RELAXAČNEJ KERAMIKY

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Článok popisuje elektrickú odozvu relaxačnej feroelektrickej keramiky pripravenej na báze $Pb(Mg_{1/3}Nb_{2/3})O_3$ s prídavkom 10 mol.% $PbTiO_3$ špecifickou metódou predprípravy oxidického prekurzoru $MgNb_2O_6$. V súčasnosti sa relaxačné feroelektriká PMN-typu s vynikajúcimi dielektrickými a elektromechanickými vlastnosťami využívajú v mnohých elektrotechnických aplikáciách, akými sú presné mikropolohovače, elektromechanické posuvné meniče, elektrostrikčné aktuátory (pri obrábaní kovov, v ink-jet tlačiarňach, vo videorekordéroch) a keramické kondenzátory. V tomto období dochádza tiež k postupnému nahrádzaniu piezoelektrických aktuátorov a senzorov v mikro-elektro-mechanických systémoch elektrostrikčnými, ktoré sa vyznačujú malými hysteréznymi stratami, vyšším rozlíšením, rýchlejšou odozvou ap. Keďže pri návrhu elektromechanických zariadení sa často v praxi požaduje ich pracovná oblasť blízko izbovej teploty (napr. ultrazvukové meniče pre diagnostické systémy v zdravotníctve), v našej práci sme sa cielene zamerali na charakterizáciu dielektrických, feroelektrických a piezoelektrických vlastností 0.9PMN-0.1PT keramiky v okolí izbovej teploty, resp. pod teplotou maximálnej dielektrickej permitivity (T_m = 46.6°C pri 1 kHz). V práci bolo experimentálne dokázané, že študovaný materiál vykazuje v teplotnej oblasti pod T_m vysokú hodnotu relatívnej dielektrickej permitivity v rozmedzí od 3000-4000. Teplota T_m je frekvenčne závislá a feroelektrický fázový prechod v pseudobinárnom perovskitovom 0.9PMN-0.1PT systéme je difúzny. Následne realizované feroelektrické, pyroelektrické a piezoelektrické merania jednoznačne preukázali, že nami pripravený elektrostrikčný materiál sa pri izbovej teplote nachádza v relaxačnom stave.

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