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GRAIN SIZE EFFECT ON THE INDUCED PIEZOELECTRIC PROPERTIES OF 0.9PMN-0.1PT CERAMIC

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Abstract: Lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$-PMN)-lead titanate ($PbTiO_3$-PT) solid solutions are widely researched to produce devices that can be used in low and high electric field applications. For some applications, such as medical ultrasonic transducers, it is necessary to prepare the ceramic with high density and small average grain size. This paper describes the effect of grain size on the low and high field properties of 0.90PMN-0.10PT ceramics. To prepare highly dense ceramic, vibratory and attrition milled powders were sintered between 1000-1250°C. The average grain sizes of the sintered ceramics varied from 0.7 to 3.5 μm. To understand the grain size effect, dielectric, pyroelectric, electrostrictive, and induced piezoelectric properties were studied.

Introduction

Relaxor ferroelectric materials are widely studied for their dielectric, electrostrictive and induced piezoelectric properties. In the past decade, these materials were used in a variety of applications ranging from multi-layer capacitors to ultrasonic transducers[1,2]. Takeuchi et al.,[2] investigated the effect of 0.90PMN-0.10PT ceramic for the medical imaging in the 1-3 configuration. Because of the high operating frequency, the dimensions of the 'cylindrical' ceramic posts are restricted to only a few tens of microns in all directions. To manufacture such posts reliably and reproducibly, it is necessary to use high density ceramic with small grain size.

The grain size effect on the low and high field properties of PMN-based ceramics has been investigated by several researchers[3-6]. In general, the properties degrade as the grain size is reduced. For example, in 0.93PMN-0.07PT ceramic, the peak dielectric constant drops from 25,000 to 5000 when the average grain size is reduced from 5 μm to 0.3 μm[5]. The size effects observed in these ceramics were attributed to the extrinsic and intrinsic effects such as pore volume, low-K grain boundary phase, and micropolar domain densities. From the literature survey, it appears that the properties of the fine grain ceramic can be improved by minimizing the effect of extrinsic variables and by improving the homogeneity.

In this paper, the effect of average grain size on the low and high electric field properties of 0.90PMN-0.10PT ceramic is reported. Ceramics with average grain sizes ranging from 0.7 to 3.5 μm were prepared from vibratory and attrition milled powders. Low field properties such as dielectric constant and high field properties such as P-E hysteresis, pyroelectric, electrostrictive and a few of the electric field induced resonance properties were investigated as a function of grain size.

Experimental

Preparation

To prepare the ceramic powder, a coulumbite precursor technique was adopted[7]. The magnesium niobate precursor was prepared by calcining the appropriate mixture of MgO(J.T. Baker, Phillipsburg, NJ) and Nb_2O_5(Transelco, NJ) at 1000°C/5h and then at 1100°C/5h. The completion of reaction and the phase purity were checked by comparing the XRD pattern with the JCPDS standard. The PMN-PT batches were prepared by calcining the appropriate mixture of PbO(Hammond, Pottstown, PA), $MgNb_2O_6$, and TiO_2 (Whittake, Clark, and Daniel, South Plainfield, NJ) powders at 900°C/5h.in a closed alumina crucible. To vary the initial average particle size, the calcined powder was subjected to the following grinding schedule. First, the powder was wet ball milled in alcohol in a nalgene bottle with ZrO_2 grinding media for 24h. After drying, a portion of the powder was vibratory milled(Sweco) for 24h. For vibratory milling, a 30 vol% slurry was prepared with water and a few drops of Tamol 901 was used as a dispersant. To minimize contamination, small yittria stabilized ZrO_2 spheres were used as milling media. To increase the surface area further, a small portion of the vibratory milled slurry was attrition milled(Reliance) for an additional 24h. The ball milled, vibratory milled, and attrition milled powders were named as batch A, B, and C, respectively. The ZrO_2 contamination level, and the B.E.T. surface area of these powders are listed in Table 1.

The dried powder was granulated with 5 wt% of Dupont 5200 binder in acetone media. After passing the mixture through a 100 mesh sieve, 1/2" dia. disks were cold pressed in a steel die with 30,000-35,000 psi uniaxial pressure. The binder from the disks was removed by a two stage heat treatment at 300°C/3h and then at 500°C/5h. These pellets were sintered in a closed alumina crucible at 1000-1250°C/1-5h. A small amount of PbO-ZrO_2 mixture was heated along with the pellets to control the lead oxide atmosphere inside the crucible. All the sintered samples were annealed at 950°C/2h. to evaporate excess PbO. The weight losses during these preparation stages were monitored accurately.

Characterization

The bulk densities of the sintered specimens were calculated by measuring the weight change in Xylene. The grain size distribution was analyzed from the microstructures of fractured and polished surfaces. The microstructures were recorded using ISI-DS130 Secondary electron microscope.

Detailed experimental descriptions of dielectric, pyroelectric, P-E hysteresis, and electrostrictive measurements can be found in Ref.8. Dielectric measurements were made on gold sputtered discs

Table 1. Properties of Powder:

	A	B	C
ZrO_2 impurity (wt%)	0.67	0.71	1.03
B. E. T.(m^2/gm) Surface Area	1.29	3.17	15.46

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while cooling from 100°C to -100°C at a rate of 2°C/min. For pyroelectric measurements, the electroded samples were cooled from 50°C to -75°C with an electric field of 10 KV/cm. After neutralizing the surface charge, the pyroelectric current was measured by heating the specimen to 50°C at 4°C/min. For P-E hysteresis and transverse electrostrictive measurements, an a. c. triangular field of ± 10 kV/cm was applied at a frequency of 0.1 Hz. The transverse strain measurements were made with a strain gauge technique. By differentiating E vs. s_2 plots, $-d_{31}$* values as a function of electric field were calculated.

AC impedance measurements were performed on circular disk samples of t < 0.3 mm with sputtered silver electrodes. Resonance curves of conductance G, and resistance R of the samples at various biases were recorded with an HP 4194A impedance analyzer at 25°C. Series and parallel resonance frequencies f_s and f_p of thickness resonance mode were used to calculate k_t with the equation given in Ref.9.

Results and Discussion

Physical Properties

The density and weight loss data of batch B and batch C samples are listed in Table 2. In general, samples sintered at lower temperatures show slightly higher density due to limited grain growth. Among the two batches, as the initial average particle size of C was lower, it sintered to comparatively higher densities. At higher sintering temperatures, as the grain growth mechanisms dominate, both batches sintered to similar densities. While batching the powders for calcination, to ensure the completion of reaction, 0.5 wt% excess PbO was added. But after sintering and annealing, higher weight losses were observed (Table 2). As reported by Wang and Scultz[6], our sample surfaces also showed a small number of pyrochlore grains. Since the pyrochlore is lead deficient in nature, excess PbO is evaporated while annealing.

The polished and fractured microstructures of a few of the sintered samples are reproduced in Fig. 1. The mean average grain sizes for all the samples are listed with standard deviation in Table 2.

Table 2. Physical Properties of the ceramic.

	Si. Tem. °C/h	wt. loss %	Density gm/cc	% Theo.	Ave. g.s. (μm)
B1	1000/1		7.28±0.04	89.24	
B2	1050/1	1.10	8.00±0.02	98.06	1.1±0.2
B3	1100/1	1.10	7.99±0.01	97.94	1.2±0.3
B4	1150/1	1.11	7.98±0.02	97.84	1.3±0.3
B5	1200/1	1.16	7.96±0.03	97.57	1.7±0.5
B6	1250/1	1.20	7.90±0.02	96.84	2.2±0.8
B7	1250/5	1.32	7.83±0.03	95.98	3.3±1.3
C1	1000/1	0.85	7.92±0.03	97.08	0.7±0.2
C2	1050/1	0.99	8.00±0.03	98.08	1.0±0.3
C3	1100/1	1.03	7.99±0.02	97.94	1.4±0.4
C4	1150/1	1.06	7.98±0.02	97.82	1.5±0.5
C5	1200/1	1.02	7.94±0.02	97.33	1.9±0.6
C6	1250/1	1.13	7.88±0.03	96.59	2.4±0.8
C7	1250/5	1.29	7.80±0.03	96.51	3.6±1.8

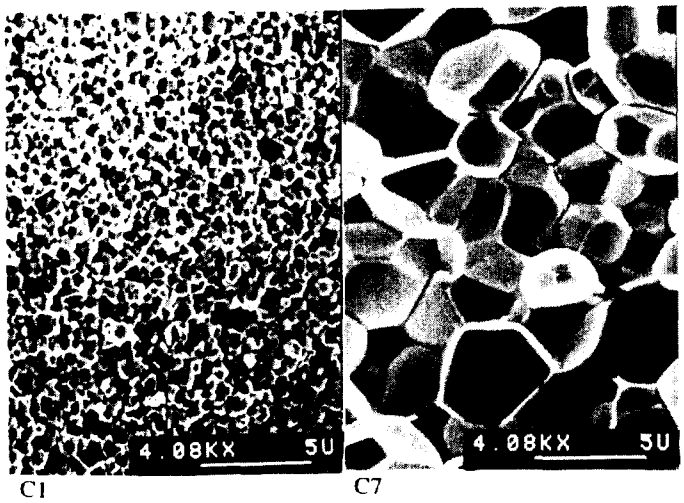

Fig.1. Fractured surfaces of C1 and C7.

Table3. Dielectric Properties of the ceramic

	g.s. μm	Kmax	Tmax °C	Tan δ at 25°C	δ (°C)
B2	1.1	17800±470	48	0.0582	40
B3	1.2	22250±050	46	0.0686	38
B4	1.3	23750±720	46	0.0718	34
B5	1.7	25300±600	45	0.0765	31
B6	2.2	28850±790	43	0.0829	27
B7	3.3	33000±550	42	0.0922	
C1	0.7	13900±300	48	0.0474	
C2	1.0	20800±360	43	0.0725	33
C3	1.4	23350±510	42	0.0792	32
C4	1.5	24700±420	42	0.0803	32
C5	1.9	25450±810	41	0.0795	30
C6	2.4	25800±720	41	0.0850	29
C7	3.6	27450±300	40	0.0891	

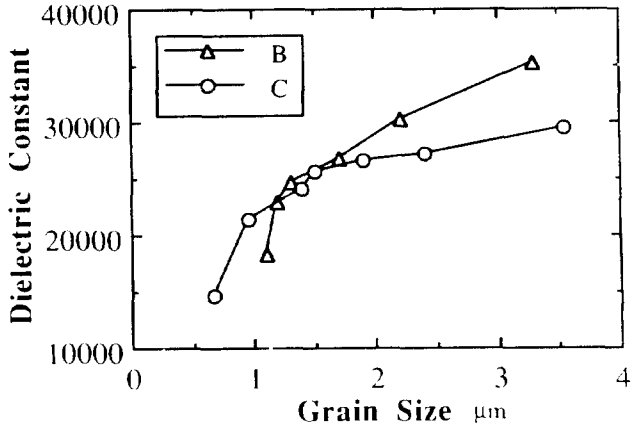

Fig.2. Effect of average grain size on K_{max}. The dielectric constant was compensated for porosity with Weiner's rule.

Low Electric Field Properties

The relevant dielectric properties are compared in Table 3. At least four samples were used to calculate the percentage change in the dielectric constant. The maximum dielectric constant (K_{max}), after compensating for porosity with Weiner's equation[10], is ploted in Fig.2, as a function of average grain size. Comparatively, the K_{max} of the samples from series B, changes as a strong function of grain size. In both batches, K_{max} reduces drastically when the grain size is <1μm.

High Electric Field Properties

The effect of grain size on the P vs. T behavior is compared in Fig. 3 and 4. To plot these figures, the polarization was calculated from the pyroelectric current. In relaxor ferroelectric materials, P vs. T behavior below the pyroelectric depolarization temperature, T_d, reflects the degree of cohesiveness among macrodomains. Below T_d, if the macrodomains are highly stable, ΔP with respect to ΔT will be small. When the material is heated, the stable macrodomains will convert into microdomains, over a narrow temperature interval around T_d. In our investigation, the samples sintered at higher temperatures show these behaviors very clearly. When the sintering temperature is reduced, increasingly large changes in P with respect to temperature is observed below T_d. More over, in these samples the macrodomains transform into microdomains over a wider temperature around T_d. Careful analysis of P vs. T behavior points out the importance of proper processing. In series C samples, as the grains were grown from finer particles, the grain size effect is minimized.

The induced polarization and the transverse strain characteristics of the fine grain samples from both batches show degradation of properties. This observation is clearly demonstrated by plotting $-d_{31}$* vs. E field, as a function of grain size (Fig. 5 and 6). These measurements were made at 25°C. When the grain size is above 3 μm, a maximum $-d_{31}$* of about 500 pC/N is observed. When the grain size is reduced, the magnitude of maximum $-d_{31}$* reduces with an increase in the corresponding electric field.

The piezoelectric thickness coupling coefficients calculated from the resonance curves observed at different d.c. biases are plotted in Fig. 7 and 8. These measurements were made at 25°C with increasing bias voltages. In both batches, coarse grained samples showed increased coupling at lower electric fields. The absolute values of coupling coefficients also increased as the grain size is increased.

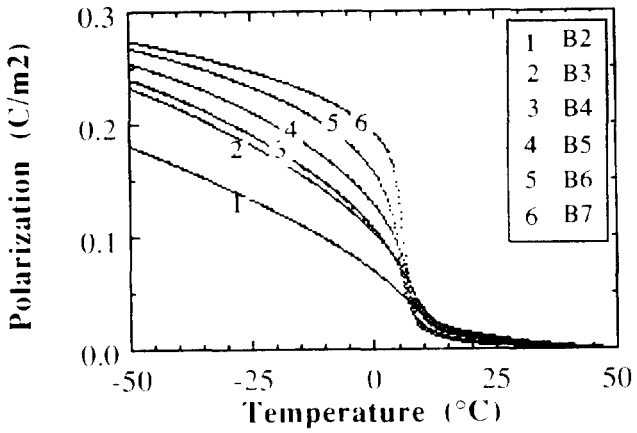

Fig.3. Polarization vs. Temperature behavior of batch B samples.

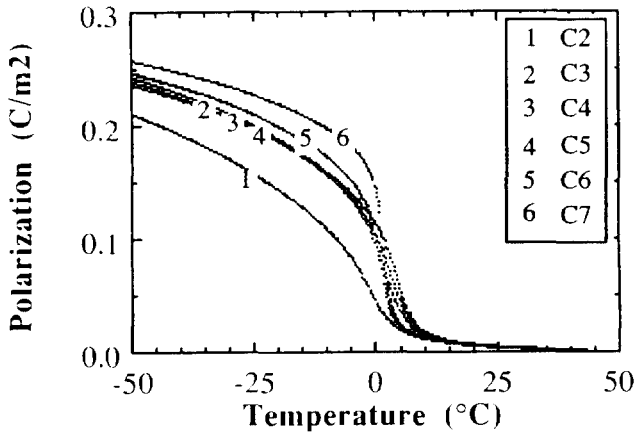

Fig.4. Polarization vs. Temperature behavior of batch C samples.

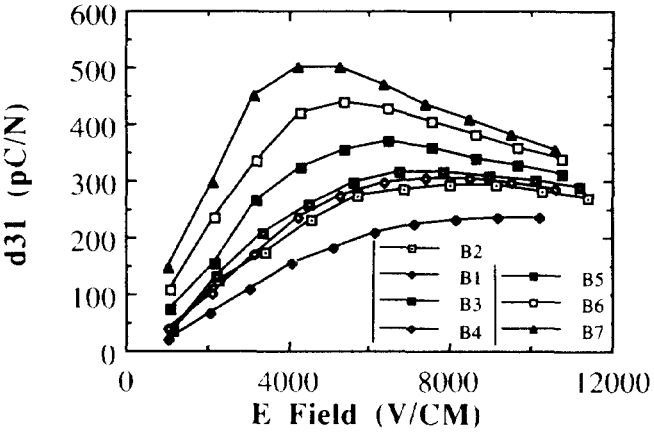

Fig.5. Effective transverse piezoelectric d coefficients of batch B samples; calculated from electrostriction data.

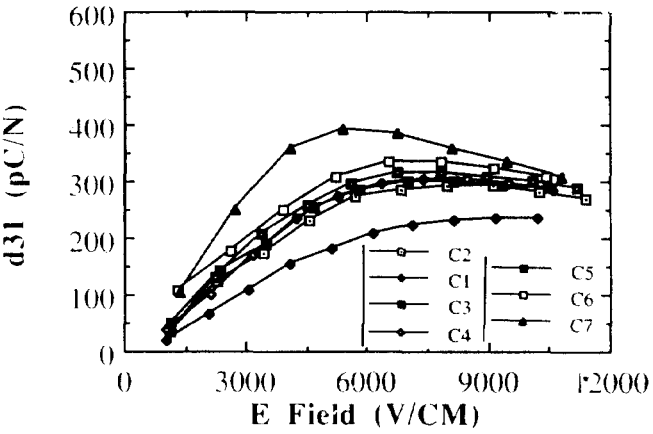

Fig.6. Effective transverse piezoelectric d coefficients of batch C samples; calculated from electrostriction data.

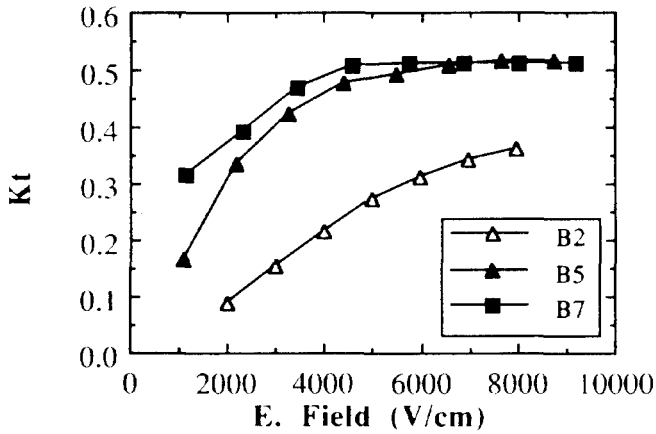

Fig.7. Thickness coupling coefficients of batch B samples at different d. c. bias fields; calculated from resonance curves.

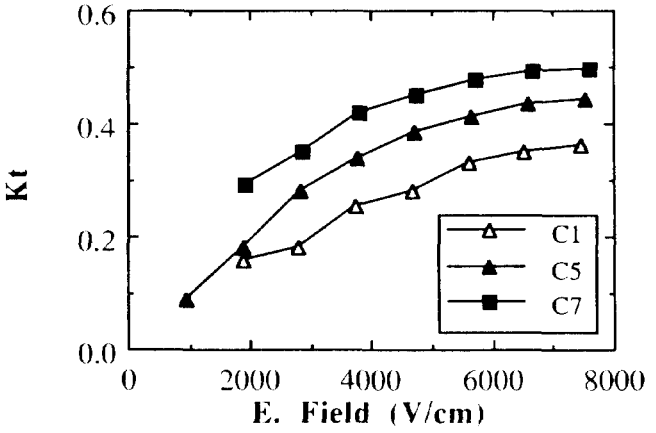

Fig.8. Thickness coupling coefficients of batch C samples at different d. c. bias fields; calculated from resonance curves.

Discussion

As mentioned in the introduction section, the grain size effect on the properties may be attributed to extrinsic and intrinsic variables. In the present samples, through careful annealing the effect of extrinsic variables are minimized. For example, B2, B3, B4 and C2, C3, C4 samples with similar weight losses and therefore with similar second phase volume at the grain boundary, show noticeable differences in the low and high electric field properties. As observed in all the properties, large grain samples with lower density show better properties as compared to fine grain samples with higher densities.

Careful analysis of the the low and high electric field properties show clear distinction between the properties of series B and series C samples. Slight depression of T_{max} and T_d in series C samples may be attributed to the higher concentration of Zr^{4+} ions as dopant[11]. Considering the average grain sizes of all these samples, ranging from approximately 0.7 μm to only 3.5 μm, it appears that the sintering temperature also influences the properties. From the surface area of the milled powders, the equivalent spherical diameter of the series B and series C powders are calculated as 0.23 μm, and 0.047 μm, respectively. Comparing the grain sizes, it is clear that the series C samples show at least 15 times growth during sintering. Because of this growth, it is hypothised that these samples are more homogeneous as compared to series B samples. Hence, the lesser influence of the average grain size on the low and high field properties of series C samples may be attributed to higher degree of homogeneity.

Conclusion

In this paper, the dielectric, pyroelectric, electrostrictive, and the induced piezoelectric properties of 0.90PMN-0.10PT ceramic are compared as a function of grain size. Comparatively, samples prepared from coarse particle compact show higher grain size dependance. When the average grain size is around 3.5 μm, irrespective of the initial powder characteristics, the ceramic show similar high electric field properties. Through transverse strain measurements, a high $-d_{31}$* of 500 pC/N at a d.c. bias of 4300 V/cm is observed. When the samples were prepared from very fine powders, the magnitudes of K_{max}, $-d_{31}$*, and k_t reduces only moderately as the grain size is reduced to 1.5 μm. Since the effect of extrinsic variables such as density and the grain boundary phase are minimized through careful preparation, the observed grain size

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