



# Substituent Effects in $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.35\text{PbTiO}_3$ Piezoelectric Ceramics

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**Abstract.**  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT) ceramics with base compositions close to the morphotropic phase boundary are potential materials for many applications such as transducers and actuators due to their high dielectric constants and electromechanical coupling factors. However, their dielectrical and mechanical losses are too high for high-power applications. In this paper, the dielectric and electromechanical properties of piezoelectric PMN-PT ceramics were investigated in specimens containing various A-site and B-site substituents with the goal of developing lower loss materials for wider applications. Emphasis was placed on various transition metal cation substituents of both lower and higher valences. Mn substituent was found to be the most promising substituent investigated for developing high power low loss piezoelectric PMN-PT ceramics.

**Keywords:** PMN-PT, substituents, dielectric and electromechanical properties

## I. Introduction

Since the discovery of relaxor behavior in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) by Smolenskii and Agronovskaya [1], many investigations of mixed B-site cation relaxor ferroelectrics, of the  $\text{Pb}(\text{BI}_{1/3}\text{BII}_{2/3})\text{O}_3$ -type perovskites, have been performed, due to their excellent dielectric and electromechanical properties. A characteristic feature of these materials is that they possess B-site cation sublattices which are occupied by ionic species of various valencies. In the stoichiometric case, charge compensation requires that the average valence of the B-site be +4, however in  $\text{Pb}(\text{BI}_{1/3}\text{BII}_{2/3})\text{O}_3$  this occurs by a mixture of higher (>+4) and lower (<+4) valent cation species on the octahedral B-site sublattice. In PMN, electron microscopy investigations by Chen and Harmer have shown the presence of short-range B-site cation ordering [2]. The size of the short-range ordered regions was observed to be ~30 to 50 Angstroms and were character-

ized by the presence of (1/2,1/21,1/2) superlattice reflections in the selected area electron diffraction patterns. Investigations by Setter and Cross [3] have demonstrated that the electrical properties of relaxor ferroelectrics are influenced to a large degree by the manner in which B-site cations (BI and BII ions) are distributed amongst the B-site sublattices. Specimens which were quenched and possessed very low B-site cation ordering had relaxor ferroelectric characteristics, whereas specimens which were annealed and possessed a high degree of B-site cation ordering had normal ferroelectric characteristics.

The structure of PMN is pseudo-cubic with an average space group symmetry of  $\text{Pm}3\text{m}$  at room temperature. The degree of short-range B-site cation ordering in PMN is quite small [3], thus the relaxor characteristics are pronounced, and the dominant electromechanical coupling mechanism is electrostriction [4]. In crystalline solutions of  $(1-x)\text{PMN}-x\text{PbTiO}_3$  (PMN-PT), a piezoelectric state with a remanent polarization can be

achieved. The PMN-PT crystalline solid solution system possesses a morphotropic phase boundary (MPB) between pseudo-cubic and tetragonal ferroelectric phases at about 30–35 at. % PT ( $T = 25^{\circ}\text{C}$ ) [5]. The dielectric and piezoelectric constants for these PMN-PT compositions ( $0.3 < x < 0.35$ ) are significantly high, as reported by many researchers such as Lejeune [6]. The high piezoelectric, dielectric, and electromechanical coupling coefficients in the MPB compositions of PMN-PT are very attractive for applications in high-power transducer devices. However, one of the limitations of PMN-PT in these applications is that the mechanical quality factor  $Q_m$  is quite low, in addition to the dielectric loss being quite high.

The purpose of this investigation was to study the effect of various substituents on the properties of PMN-PT ceramics. It was hoped that a trend in the substituent types and classes might be identified, so that a wider range of materials might be developed for high power transducer applications. Both A-site and B-site substituents, as well as higher and lower valent substituents, have been investigated.

## II. Sample Preparation and Experimental Procedure

In order to eliminate the formation of a parasitic pyrochlore phase ( $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ ), the columbite precursor method proposed by Swartz and ShROUT [7] was used to prepare PMN-PT 65/35 ceramics. In the first stage, MgO and  $\text{Nb}_2\text{O}_5$  were mixed in a stoichiometric ratio, and a precursor columbite phase  $\text{MgNb}_2\text{O}_6$  was formed after calcination at  $1200^{\circ}\text{C}$  for 4hrs. (X-ray diffraction patterns were then taken to check phase formation). In the second stage, the precursor was mixed in stoichiometric ratios with PbO and  $\text{TiO}_2$ . To insure proper mixing, both steric hinderance and electrostatic repulsion (pH adjustment by ammonia), dispersion mechanisms were required to prepare a 30 vol.% slurry with de-ionized water. The slurry was vibratory milled, then dried and calcined at  $700^{\circ}\text{C}$  for 4 hr. Calcined powders were examined by x-ray diffraction to insure phase purity. To control PbO volatility, sintering was performed in a lead rich atmosphere by placing a small amount of mixed powder of PbO and  $\text{ZrO}_2$  in a closed crucible. Sintering was performed at  $1000\text{--}1200^{\circ}\text{C}$  for 4 hours depending on the different doping elements and concentration.

Specimens with both A-site and B-site substituents,

including higher valence and lower valence ones, were fabricated. The various substituents investigated include La, Li, Na, K, Mn, In, Fe, Cu and Co. Specimens with excess Mg and Nb were also fabricated for comparisons. For each composition, two batches were prepared and at least three samples were made and measured from each batch. After sintering, the samples were polished, and gold-sputtering was used for the electrodes on both surfaces.

The dielectric properties were measured with a computer controlled automated-measurement system (HP4284A) from room temperature to  $250^{\circ}\text{C}$  for dielectric measurement in an oven with temperature controlling (FLUKE8840). The electromechanical properties were determined with the resonance-antiresonance method by measurement of the admittance spectrum using a HP4194.

## III. Results and Discussions

Table 1 summaries the dielectric and electromechanical properties of PMN-PT 65/35 with 1 at.% of various A-site substituents. Data taken from previous studies of various substituents in PZT, and the radii of  $\text{Pb}(2+)$  and  $\text{Ti}(4+)$ , have also been included in this table [8].  $\text{La}(3+)$  has previously been studied in PMN and PMN-PT [9], as well as in PZT [10]. In La modified PMN-PT, it was found that lead vacancies are not a favorable defect, unlike that in PZT [9]. PMN prefers to restore the A/B ratio by precipitating out magnesium niobate. Compensation is thus achieved by self-adjustment of the Mg/Nb ratio.

The effects of Na and K substituents can be seen to be almost the same in Table 1. Both substituents are from the same element group (s-orbital with a 1+ valance state) and substitute onto the  $\text{A}^{2+}$  (Pb) sites, which are 12-fold coordinated. Hence, they effectively act as acceptors. It is necessary to charge compensate for a  $\text{Na}^{1+}$  occupying a  $\text{Pb}^{2+}$  site. This was achieved by reducing the Mg:Nb ratio. Consequently, these substituents should decrease the degree of short-range B-site cation ordering, as previously reported by Chen and Harmer [4]. Both of these substituents were found to somewhat increase the mechanical quality factor  $Q_m$  and reduce the piezoelectric constant, as shown in Table 1. Temperature dependent dielectric constant data are shown in Fig. 1 (b) for these composition.

Li is also from the same chemical group (s-orbital with a 1+ valance state), yet the effect of Li on the di-

Table 1. Electromechanical properties of 0.65PMN-0.35PT + 1 at.% A-site Doping.

Element	La	K	Na	Li
Substitute site	A-site	A-site	A-site	
Valency	+3	+1	+1	+1
Behavior in PZT	Donor-like	Acceptor-like	Acceptor-like	?
Ionic radii (Å)	1.20	1.52	1.16	0.90
Density (g/cc)	7.95	8.10	8.02	7.81
Curie T (°C)	149.40	181.23	178.00	178.29
Dielectric constant (1kHz)	3700	3990	4140	3260
Maximum dielectric constant (1kHz)	16000	34800	34800	25600
Dielectric loss (1kHz)	0.031	0.012	0.011	0.031
$s_{11}^E$ ( $10^{-9}$ m <sup>2</sup> /N)	0.015	0.013	0.014	0.020
$k_{31}$	0.220	0.280	0.278	0.310
$d_{33}$ (pC/N)	340	373	360	546
$Q_m$	64	143	150	68
	Used to adjust Curie temperature			Used to improve the electrical resistance, reduce the sintering temperature and reduce the temperature coefficient of capacitance

Pb (+2) 1.330Å, Ti (+4) 0.745Å

A-site cation : 12-coordinated

B-site cation : 6-coordinated

electric and electromechanical properties were significantly different than those for Na and K, as can be seen in Table 1. Li substitution also reduced the sharpness of the temperature dependent dielectric constant, as can be seen in Fig. 1. The ionic radius of Li is smaller (0.90Å) than that of either Na (1.16Å) or K (1.52Å). However, according to the tolerance factor

$$t = \frac{(r_{A(12-CN)} + r_{O(6-CN)})}{\sqrt{2}(r_{B(6-CN)} + r_{O(6-CN)})}$$

Li still is too large for it

to go onto the B-sites. Table 2 summarizes the properties of B-site substituents. Indium is the only non-transitional metal cation listed in this table. Indium substitution resulted in the highest electromechanical coupling (0.36) and one of the highest piezoelectric (571 pC/N) coefficients. The ionic radius of In<sup>3+</sup> is quite large (0.94). Interestingly, Pb(In<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> exists a stable mixed B-site cation perovskite, which is known to be a relaxor antiferroelectric[11].

As shown in Table 2, four transition metal cations were chosen as substituents. Interests were placed on these substituents because transition metal cations often have multiple valence states. For example, in the

PZT system, Fe is known to increase  $Q_m$  to more than 1000 [12]. Analogously, it was hoped that Fe-substituents might have a similar effect in PMN-PT, however this was not the case. Fe-substituents were found not to change the properties of PMN-PT significantly. In PZT, all B-site cation sites are occupied by 4+ species. Whereas, in PMN-PT, two distinct B-site cation sublattices exist whose occupancies are composed of multiple valent species, i.e., 2+ (Mg), 5+ (Nb), and 4+ (Ti). In consideration of the ionic size of Fe, it will most probably substitute onto the Mg sites in PMN-PT, rather than the Nb ones. If this is the case, then Fe is either a 3+ (or 2+) species on a 2+ site. It will then act either as an isovalent or as a donor-type substituent, rather than an acceptor-type one as it does in PZT. Consequently, the electromechanical properties of Fe-substituted PZT and PMN-PT will be different. Fe-substituted PZT will be a “hard” piezoelectric, whereas Fe-substituted PMN-PT will be a “soft” piezoelectric.

Similar arguments can also be used to understand the effects of Co-substituents, which have a smaller ionic radius than Fe. Again, based on the ionic radius consideration, Co<sup>2+</sup> and/or Co<sup>3+</sup> will most probably

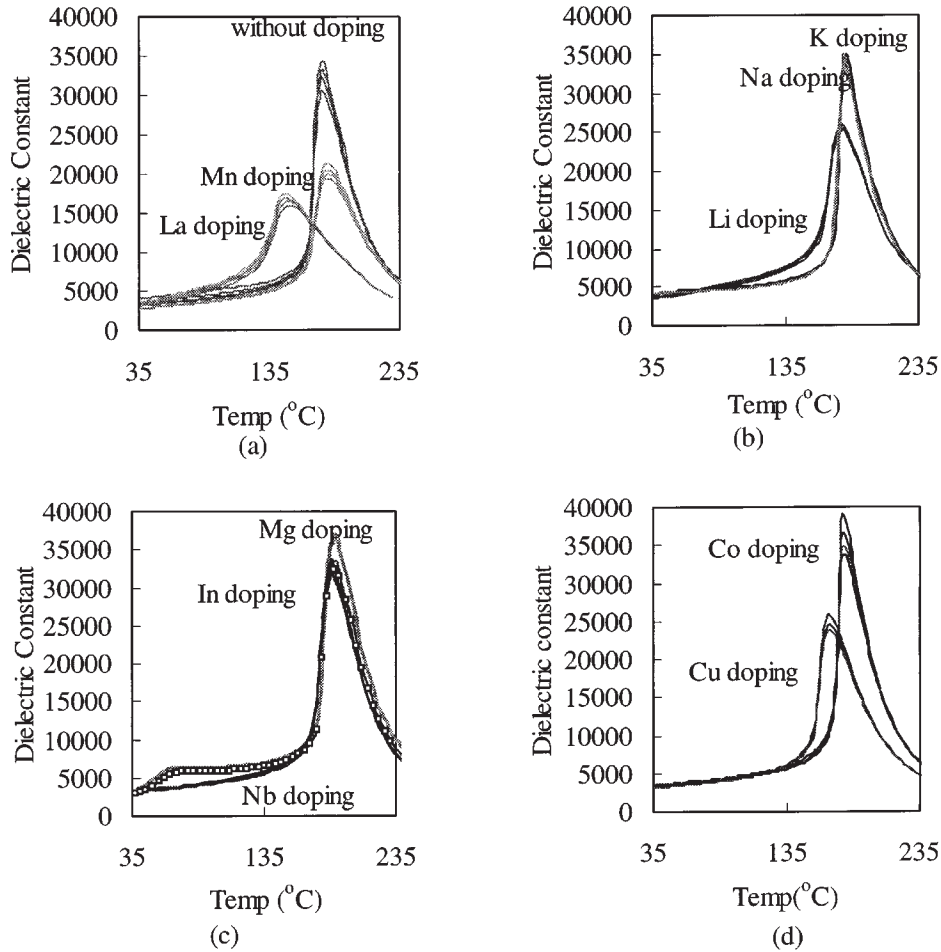


Fig. 1. The temperature and frequency dependence (100, 1k, 10k, 100k from high to low) of dielectric constant of 0.65PMN-0.35PT + 1 at.% (a) pure and La, and Mn; (b) Li, Na, and K; (c) In, Mg and Nb; (d) Co and Cu.

substitute onto the Mg sites. Co also has an additional valance state (+4) which has a smaller ionic radius ( $0.67\text{\AA}$ ). This valance state is not common, but it is accessible. Consequently, it may be possible for Co to go onto the Nb site and behave as an acceptor. This would result in “harder” piezoelectric characteristics. Interestingly, Co-substituent resulted in higher values of  $Q_m$  ( $\sim 152$ ) and lower values of dielectric losses (0.008) ( $Q_e \sim 125$ ), as can be seen in Table 2. But, yet, Co did not result in any significant decrease in either the piezoelectric or dielectric constants, as would be expected of a “harder” piezoelectric response.

The ionic radius of copper is significantly larger than that of the other substituents investigated. Interestingly,  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$  are too small for the A-site, but yet too big for the B-site. However,  $\text{Cu}^{3+}$  is of the

right ionic size and maybe suitable for substitution onto the Nb sites. If this were the case, then Cu substituents should act as an effective acceptor in PMN-PT, making the piezoelectric characteristics “harder”. Cu substituents resulted in a much lower value of the dielectric loss (0.004,  $Q_e \sim 250$ ). Interestingly, its mechanical quality factor was not increased dramatically, furthermore the piezoelectric constant was significantly increased ( $\sim 570$  pC/N). Temperature dependent dielectric data (Fig. 1(d)) revealed a decrease in the peak dielectric constant and a decrease in the phase transition temperature.

Of all the substituents investigated in this study, Mn was the only one which was found to impart “harder” characteristics in both the dielectric and electromechanical properties. As shown in Table 2, upon Mn

Table 2. Dielectric and electromechanical properties of 0.65PMN-0.35PT+1at.% B-site doping.

Element	Cu	Co	Mn	Fe	In
Substitute site	B-site	B-site	B-site	B-site	B-site
Valency	+1, +2	+2, +3	+2, +3, +4, +7	+2, +3	+3
Behavior in PZT	Acceptor-like	Acceptor-like	Acceptor-like	Acceptor-like	Acceptor-like
Ionic radii(Å)	(+1)0.91 (+2)0.87	(+2,LS)0.79 (+2,RS)0.89 (+3,LS)0.69 (+3,RS)0.75	(+2,LS)0.81 (+2,HS)0.97 (+3,LS)0.72 (+3,HS)0.79 (+4)0.67 (+7)0.60	(+2,LS)0.75 (+2,HS)0.92 (+3,LS)0.69 (+3,HS)0.79	0.94
Density (g/cc)	8.04	7.45	7.67	7.70	7.72
Curie T (° C)	166.98	177.00	175.00	178.00	187.62
Dielectric constant (1kHz)	2500	3200	2100	3100	3140
Maximum dielectric constant (1kHz)	23600	33600	21000	33000	33400
Dielectric loss (1kHz)	0.004	0.008	0.009	0.012	0.012
$s_{11}^E$ ( $10^{-9}\text{m}^2/\text{N}$ )	0.012	0.013	0.011	0.015	0.018
$k_{31}$	0.25	0.26	0.29	0.30	0.36
$d_{33}$ (pC/N)	571	499	350	500	564
$Q_m$	132	152	300	80	88
		Can form PCN	1. Used as similar reason of Li. 2. Change the age effect.	Can form PFN	Can form PIN

LS: Low spin

HS: High spin

modification, the piezoelectric constant, dielectric constant and dielectric loss were all decreased, however the quality factor  $Q_m$  was increased significantly. The coupling coefficient  $k_{31}$  was not significantly affected by Mn modification and had a constant value of  $\sim 0.3$ . Due to the many valent states available to Mn (which range from +2 to +7), it is difficult to ascertain based upon simple crystal symmetry arguments which sites Mn most probably occupies. The data presented in Table 1 indicates that whichever site Mn does occupy it is acting as a lower valent species on a higher valent site. Furthermore, the changes in properties that occur upon Mn modification make the material more suitable for high power transducer applications.

Beck et al. have previously investigated Mn-substituted PMN-PT [11]. They studied specimens modified with 1 at.% Mn in a base composition of PMN-PT 95/5. This base composition has pronounced relaxor ferroelectric behavior, however addition of 1 at.% resulted in a conversion of the dielectric response into a

normal, non-dispersive ferroelectric [13]. Mn substitution has been found to induce unique changes not only in PMN-PT, but also in BaTiO<sub>3</sub>. In BaTiO<sub>3</sub>, Mn substituents influence the orthorhombictetrahedral ferroelectric transition [14]. It was conjectured that a mixed Mn valent state (Mn<sup>3+</sup> and Mn<sup>2+</sup> coexisting) de-stabilizes the orthorhombic phase at a temperature  $T_2$ . Similarly, a combination of Mn<sup>4+</sup> and Mn<sup>3+</sup> was conjectured to be responsible for the destabilization of the rhombohedral phase at a temperature  $T_3$ , for specimens that had been treated under higher oxygen partial pressures during densification. Lattice distortion caused by Mn ions appeared to be a factor in this case [15].

Table 3 shows data for specimens prepared with excess Mg and Nb. Neither excess Mg nor excess Nb resulted in any significant effects on the properties. Variations in the ratio of the octahedral site occupancies within a single-phase would be equivalent to aliovalent substituent modification. An excess of the lower-valent constituent, i.e., Mg<sup>2+</sup> in PMN, would be

Table 3. Dielectric and electromechanical properties of 0.65PMN- 0.35PT with 1 at.% Mg or Nb excess.

Element	Nb	Mg			
Substitute site	B-site	B-site	Maximum dielectric constant (1kHz)	33600	38100
Valency	+5	+2	Dielectric loss (1kHz)	0.024	0.020
Behavior in PZT	Donor-like	Acceptor-like	$s_{11}E$ ( $10^{-9}m^2/N$ )	0.020	0.019
Density (g/cc)	7.82	7.66	$k_{31}$	0.296	0.281
Ionic radii(Å)	0.64	0.72	$d_{33}$ (pC/N)	583	540
Curie T (°C)	185.90	189.00	$Q_m$	75	78
Dielectric constant (1kHz)	4050	3500		Form pyrochlore	Sintering aid but grain growth

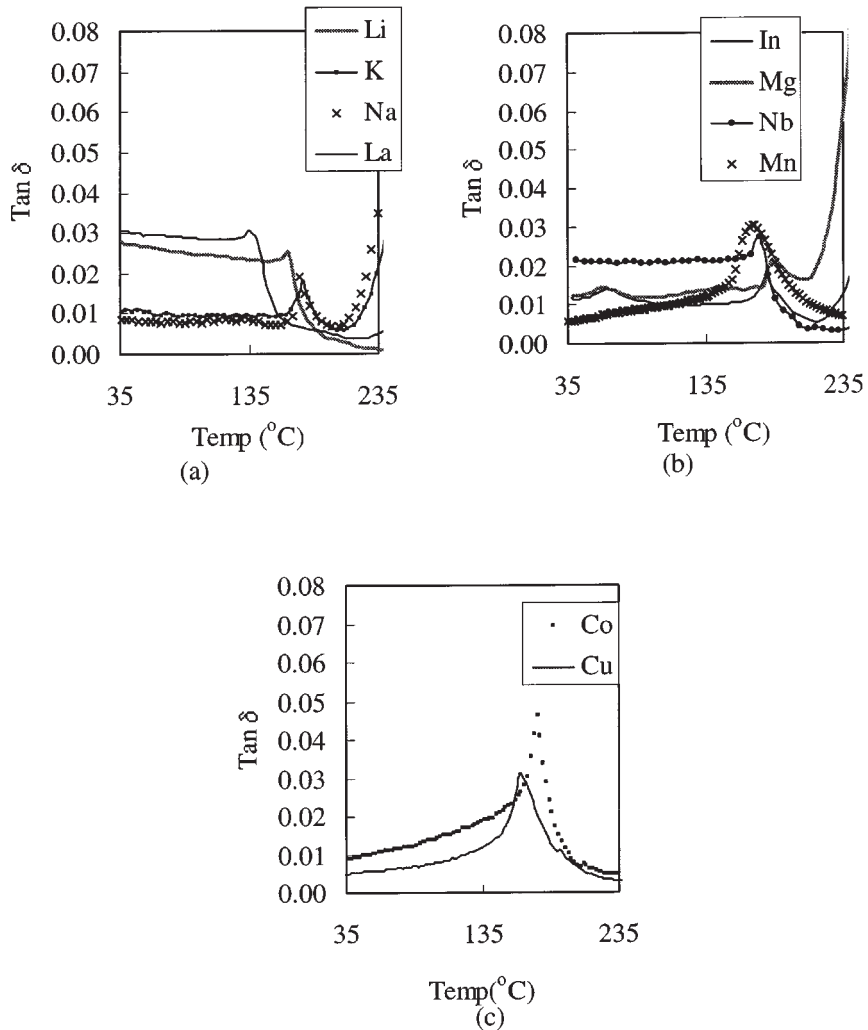


Fig. 2. The temperature dependence of  $\tan \delta$  at 1kHz of 0.65PMN-0.35PT + 1 at.% (a) pure and La, and Mn; (b) Li, Na, and K; (c) In, Mg and Nb; (d) Co and Cu.

the equivalent to lower valent substitution on a higher valent site (effective acceptor). Whereas, an excess of the higher-valent constituent, i.e.,  $\text{Nb}^{5+}$  in PMN, would be the equivalent to a higher valent substitution on a lower valent site (effective donor). However, we found that control of the Mg/Nb stoichiometry is difficult to achieve in practice, in particular with respect to changing the electromechanical properties (i.e., “harder” and “softer”). Variations in the Mg/Nb ratio tended to result in secondary phase formation in PMN-PT, instead of inducing lattice vacancy formation. However, excess MgO can be seen in Table III to increase the dielectric constant. This may be due to the excess MgO reacting with pyrochlore on the grain boundaries.

Temperature dependent dielectric loss data are shown in Fig. 2 for the various specimens investigated in this study. Specimens with excess Mg and those modified with Na, In or K had significant losses at high temperatures. This kind of loss usually is contributed by the conduction loss [15]. However, specimens with Mn, Co, and Cu resulted in decreased dielectric losses at all temperatures except near the Curie temperature. In each case the dielectric loss factor had a pronounced peak near the temperature of the dielectric constant maximum. These results again indicate the importance of transition metal cation modifications on the properties of PMN-PT.

#### IV. Summary

In this paper, MPB compositions of PMN-PT with various substituents were studied. Unlike previous results for PZT, the effect of substituents on the mechanical quality factor was quite small. However, Mn substituents were found to be unique. Mn substituents

were found to reduce the total loss (including mechanical and dielectric) while keeping the electromechanical quality constant. These changes make PMN-PT more suitable for high-power transducer. It appears that Mn substituents behave as effective acceptors in PMN-PT ceramics, resulting in “harder” piezoelectric characteristics.

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