

Influence of Sintering Time on Electrical Properties, Densification, and Microstructure of PMN-PT-PMS Piezoelectric Ceramics

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Abstract

The effect of sintering soaking time on the dielectric, piezoelectric, and structural properties of PMN-PT-PMS [Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃-Pb(Mn_{1/3}Sb_{2/3})O₃] ceramics was systematically investigated. High density samples were prepared using solid-state sintering technique with different soaking times (60-150 min). Rhombohedral perovskite structure was the dominant phase for all soaking times, confirmed by XRD analysis. However, the pure perovskite structure could not be preserved at sintering times over 120 min. SEM micrographs indicated that homogeneous microstructures were obtained for all soaking times and the grain and pore sizes increased slightly with longer sintering time. Dielectric and piezoelectric test results showed that the optimum value of dielectric constant, electromechanical coupling factor, and piezoelectric strain coefficient was obtained for PMN-PT-PMS when sintered for 90 min. Ceramic samples with high density and perovskite structure prepared by proper sintering condition yielded high dielectric and piezoelectric response.

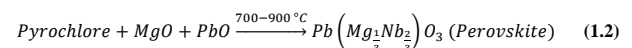
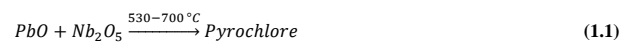
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1. Introduction

Electronic ceramics have been used for a wide range of applications since the 20th century with the discovery of high dielectric constant materials. Ferroelectrics, a subgroup of electronic ceramics, are preferred in many important applications such as underwater imaging, communication, and medical imaging devices, owing to their different functional properties [1].

The relaxor Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) is a ferroelectric material with good voltage stability, low sintering temperatures (<1000 °C), and high dielectric characteristic at Curie temperature (T_c). However, the Curie temperature of this material is around -15 °C, which limits its use [2]. With the addition of PbTiO₃ (PT), which has normal ferroelectric properties and a high Curie temperature (~ 490 °C), the phase transformation temperature of PMN reaches higher values, thus increasing its usage areas.

(1-x)PMN-(x)PT solid solution, with perovskite crystal structure, forms a morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases at approximately x=0.325 at room temperature. Compositions in the vicinity of MPB exhibit optimum dielectric, ferroelectric, and piezoelectric properties [3]. Unlike other ferroelectric ceramics, compositions containing lead and niobium (such as PMN-PT) cannot be easily obtained in the perovskite structure by conventional calcining of the oxide raw material mixture. The reactions that occur during the calcination process used for PMN production are as follows [4, 5]:



Since reaction-2 is not exactly balanced, the unwanted pyrochlore phase cannot completely transform into the perovskite phase. While the Pb/Nb ratio is 1.5 in the perovskite phase, this ratio is generally less than 1.5 in the pyrochlore phase [6-9]. Hence, the product obtained

as a result of the abovementioned reactions is a mixture of perovskite and pyrochlore phases. The pyrochlore phase, which has a very low Curie temperature ($-70\text{ }^{\circ}\text{C}$) and low dielectric constant, negatively affects the dielectric and electromechanical properties of ferroelectric ceramics containing pyrochlore [5]. Although $(1-x)\text{PMN}-(x)\text{PT}$ ($x=0.30-0.40$) compositions close to the morphotropic phase boundary have high piezoelectric and dielectric parameters, their mechanical quality factors (Q_m) are low and dielectric and mechanical losses are quite high. One of the effective methods for improving the electrical properties, preventing the formation of undesired pyrochlore phase, and obtaining a pure perovskite structure is appropriate doping of the basic PMN-PT composition. An example of these doping agents is $\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$ (PMS). In previous studies, it was determined that Mn and Sb doping increased the properties of PMN-PT piezoelectric ceramics such as dielectric constant (K^T) and Q_m [10]. In another study conducted by Takahashi et al. [11], the electrical properties and the densities of PMN-PT-PMS systems were examined. They demonstrated that the electrical properties of PMN-PT ceramics can be modified in a wide range with changing amount of PMS additive. Increasing amount of PMS caused the resulting ceramic to transform from a soft material to a hard one (low piezoelectric constant (d_{31}) and high mechanical quality factor (Q_m)). In a previous study conducted by Aydın and Kalem [12], the effect of PMS addition in 67PMN-33PT composition was examined. 6 mol% PMS addition yielded the optimum dielectric and piezoelectric properties ($K^T=4652$, $\tan\delta=2.6\%$, $d_{33}=255\text{ pC/N}$, $k_p=0.422$, $Q_m=210$, and $T_C=146\text{ }^{\circ}\text{C}$). Sintering parameters, along with the doping process, are also known to have a significant effect on the structural and electrical properties of both lead-based and lead-free piezoelectric compositions. This effect is greater in compositions containing volatile elements such as potassium, sodium, lead, and bismuth [13-18]. In this study, to examine the effect of sintering time, 67PMN-33PT piezoelectric ceramics with 6 mol% PMS additives were sintered for different soaking times between 60-150 minutes. In order to obtain samples with high density and perovskite structure, excess MgO and a single calcination step were used. It was previously demonstrated that this method successfully prevented the formation of the pyrochlore phase [12]. Ceramic samples obtained were characterized in terms of structural and electrical properties to reveal the relationship between sintering time and microstructure, physical and electrical properties.

2. Materials and Methods

2.1. Preparation of Ceramic Powders

Within the scope of this study, polycrystalline PMN-PT-PMS piezoelectric ceramic samples were produced using the solid-state synthesis method. Excess MgO was

added to the composition to prevent the formation of undesired pyrochlore phases in the structure. For each $0.94[0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3]-0.06[\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3]$ composition prepared, an extra 5% MgO per mole was added. PbO (Alfa Aesar, 99.9%), MgO (Sigma-Aldrich, 99%), Nb_2O_5 (Alfa Aesar, 99.5%), TiO_2 (Sigma-Aldrich, 99%), MnO (Sigma-Aldrich, 99%) and Sb_2O_3 (Alfa Aesar, 99%) powders were used as raw materials.

Oxide powders weighed for the selected PMN-PT-PMS composition were milled in a ball mill for 10 h to reduce the powder size and provide a homogeneous mixture. Grinding process was carried out at a mixing speed of 200 rpm in a polyethylene container containing ZrO_2 balls with 5 mm diameter and 99% purity ethanol. The ground powders were left to dry at $90\text{ }^{\circ}\text{C}$ for 24 h, and the resulting homogeneous powder mixture was pressed into pellets in a uniaxial dry press at 90 MPa pressure. Samples were calcined in a muffle furnace at $850\text{ }^{\circ}\text{C}$ for 2 h. After the calcination, pellets were crushed to powder form in an agate mortar and ground in the ball mill for further 24 h. 5 wt% PVA ($[\text{CH}_2\text{CH}(\text{OH})]_n$, $M_n=6000$) was added as a binder to the ground powders. Green ceramic discs, each measuring 16 mm in diameter were prepared using the plasticized powders. Compaction of the disc samples were done by uniaxial pressing under a load of 100 MPa. Binder in the disc samples was burnout by firing them at $600\text{ }^{\circ}\text{C}$ for 1 h in ambient atmosphere without any gas flow. Samples were sintered in a muffle furnace by soaking them at $1175\text{ }^{\circ}\text{C}$ for different time (60, 90, 120, and 150 min). Sintering temperature of $1175\text{ }^{\circ}\text{C}$ was selected since it provided the best piezoelectric and dielectric performance for the PMN-PT-PMS composition in this study [13]. A closed crucible assembly was used which contained the base powder bedding to inhibit Pb evaporation during sintering.

2.2. Characterization

The densities of the sintered samples were determined using the Archimedes' principle. The liquid medium used for this purpose was Xylene ($\rho = 0.88\text{ g/cm}^3$). Bruker D8 Advance model X-ray diffractometer (XRD) was used to examine the phase formations of sintered samples. Measurements were carried out with a scanning speed of $2^{\circ}/\text{min}$, in the range of $2\theta=20-60^{\circ}$ and using $\text{Cu-K}\alpha$ radiation. Microstructural examination of the produced samples was carried out using FEI Nova Nano 430 FEG scanning electron microscope on thermally etched surfaces. The samples were given a thermal etch at $1000\text{ }^{\circ}\text{C}$ for 1 h in air atmosphere. During etching, samples were enclosed using alumina crucibles to compensate for Pb loss.

For electromechanical characterization, the parallel surfaces of the sintered samples were first sanded with 1000 grit SiC sandpaper, then the sample surfaces were

electroded with silver paste and fired at 700 °C for 1 h. Electroded samples were placed in 120 °C silicone oil and poled under a 2 kV/mm electric field for 15 min. Dielectric properties such as free dielectric constant (K^T) and loss tangent ($\tan \delta$) were determined by measuring capacitance and loss factors under 1 kHz frequency by impedance analysis method (Hioki IM-3570 LCR meter). Planar electromechanical coupling (k_p) and mechanical quality (Q_m) factors were calculated through resonance-antiresonance characteristics determined via impedance analyzer (HP 4194A impedance analyzer). Piezoelectric constant (d_{33}) measurement was carried out using a Berlincourt d33-piezometer.

3. Results and Discussion

Density results of PMN-PT-PMS samples produced using different sintering times are given in Table 1. Density calculation was made by taking the average of the density values of 3 samples for each sintering time. Theoretical density value, calculated via the XRD data of the PMN-PT-PMS composition, was 8.18 g/cm³. High density samples with more than 96% of the theoretical density (T.D.) were obtained at all sintering times. These high-density values are adequate for electrical measurements to be made. However, with the increase of sintering time, the density first increased, reached its highest value for 90 minutes of sintering time, and then decreased. Too long sintering times can result in PbO losses and growth of large grains which in turn lead to formation of porosity. Thus, the density decreases. The results revealed that sintering time significantly affected the densification of PMN-PT-PMS ceramics. Lowering of densification at longer soaking times can negatively alter the piezoelectric and dielectric performance.

Table 1. Density and average grain size values of PMN-PT-PMS samples sintered at 1175 °C.

Soaking time (min.)	ρ_{measured} (g/cm ³)	ρ_{relative} (%T.D.)	Average Grain Size (μm)
60	7.89	96.5	3.8
90	8.03	98.2	4.3
120	8.01	97.9	4.5
150	7.98	97.5	5.1

XRD patterns of PMN-PT-PMS ceramics sintered at different times are given in Figure 1. Experimental diffraction lines of a PMN-PT ceramic with MPB composition consist of three separate peaks between 44° and 46° (2 θ). Two of these peaks - one of which is approximately half the intensity of the other - belong to the tetragonal phase, and the central peak between these two peaks belongs to the rhombohedral phase. To clearly understand the effect of sintering time on the phase structure, XRD pattern with the range of 44–46° was magnified and given as an inset of Figure 1. Since

all the patterns in Figure 1 have single peak in the mentioned 2 θ range, it was concluded that the perovskite structure in all samples had rhombohedral symmetry. It was previously reported that the transformation to rhombohedral symmetry occurred in PMN-PT ceramics with the addition of PMS [12]. No secondary phase was observed in the XRD patterns of the samples sintered at 1175 °C up to 120 min soaking time. However, when the time is increased to 150 minutes, the pyrochlore phase emerges as a secondary phase. Formation of the pyrochlore may be due to the increase in the volatility of lead oxide during long sintering times and, as a result, the deterioration of the stoichiometry of the composition with perovskite structure. The emergence of the secondary phase upon longer sintering has also been reported for other lead-based piezoelectric ceramic compositions [19]. XRD analyzes revealed that long sintering times have a negative effect on the phase structure of PMN-PT-PMS ceramics and cause the formation of the undesired pyrochlore phase.

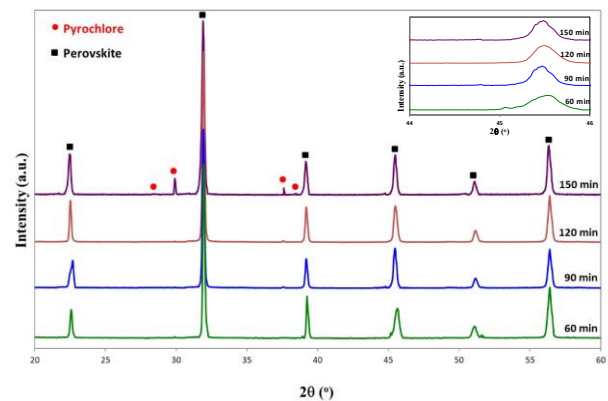


Figure 1. XRD patterns of the sintered samples with different soaking times.

The sintering process affects not only the density values and the crystal structure, but also the microstructure of the ceramics. SEM images of samples sintered at 1175 °C for different periods of time are given in Figure 2. A dense structure is observed in all samples. Increasing sintering time causes a slight increase in average grain size (Table 1). However, as shown in Figure 1, the increase of the amount and size of pores in long sintering times cause the density values to decrease in sintering conditions over 90 minutes. The grain size distribution, especially for the samples sintered for 90 and 120 minutes, is rather wide. Small grains fill the spaces between the larger ones, which resulted in high density values (Table 1).

Variation of density, crystal structure, and microstructure depending on the sintering time also significantly affected the electrical properties of the samples. Dielectric and piezoelectric properties of samples produced at different soaking times are given in Table 2. Values in Table 2 were the average values of

the electrical parameters of 3 samples for each sintering time. Dielectric constant (K^T), piezoelectric strain coefficient (d_{33}), and electromechanical coupling factor (k_p) values reached their highest values within 90 min of sintering time. The high density as well as homogeneous and pyrochlore-free microstructure obtained during this sintering period enabled high electrical properties to be obtained. Another reason for the high dielectric constant value is the presence of the rhombohedral structure alone. In PMN-PT based ceramics, PMN-rich (rhombohedral dominant) compositions exhibit higher dielectric constant values compared to PT-rich compositions (tetragonal dominant) [20]. Since 60 min-sintering resulted in a lower density value compared to longer times, the electrical properties obtained during this period were lower than others. The high density and pure perovskite structure obtained at sintering times of 90 and 120 min appeared as a positive effect on electrical properties. Although high density was also achieved in the 150 min sintering time, the existence of the pyrochlore phase during this sintering time negatively affected the mentioned electrical properties.

One of the most important factors affecting the dielectric and piezoelectric behavior of a piezoelectric ceramic is grain size. Increasing grain size is generally accompanied by an increase in the domain size and, as a result, the domain boundaries per unit volume of the sample decrease [21]. These boundaries restrict domain wall movement, and as the grain size decreases, domain wall movement becomes more inhibited. Mechanical quality factor (Q_m) and loss tangent ($\tan \delta$) values were not directly affected by the density change, unlike other parameters given in Table 2. In the change of these parameters, the effect of grain size is more dominant. The slight increase in grain size with increasing

sintering time facilitated the domain boundary movement, which in turn caused an increase in dielectric losses and a slight decrease in mechanical quality factor values. All experimental results in this study revealed that electrical parameters in piezoelectric ceramics and in general in all ceramic materials used in electronic applications can be improved by sintering conditions, in addition to effects such as doping and sintering additives. The electrical parameters obtained in this study are competitive or better than those of similar compositions reported in the literature, as shown in Table 3.

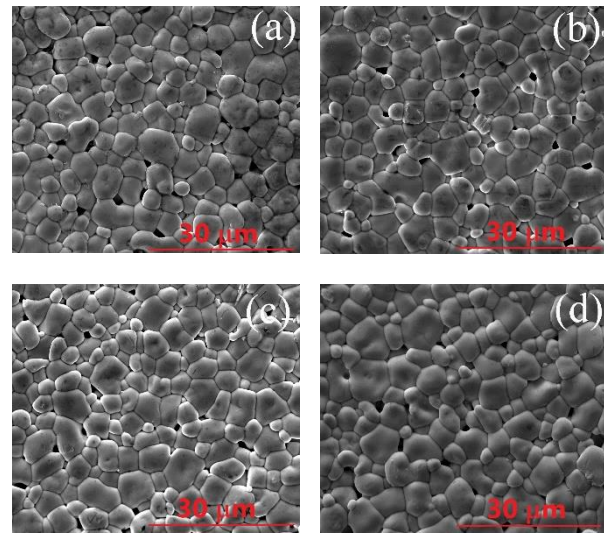


Figure 2. SEM micrographs of PMN-PT-PMS samples sintered for different soaking time: (a) 60, (b) 90, (c) 120, and (d) 150 min.

Table 2. Dielectric and piezoelectric properties of PMN-PT-PMS samples.

Soaking time (min.)	K^T	$\tan \delta$ (%)	d_{33} (pC/N)	Q_m	k_p
60	4422±19	2.4±0.05	257±9	230.1±1.1	0.409±0.004
90	4800±22	2.5±0.04	270±10	229.7±2.2	0.418±0.004
120	4745±18	2.5±0.05	265±7	222.0±2.1	0.417±0.003
150	4588±27	2.7±0.03	245±7	210.5±2.2	0.417±0.003

Table 3. Comparison of the optimum electrical properties in this study with similar compositions reported in the literature.

Reference	Composition	K^T	$\tan \delta$ (%)	d_{33} (pC/N)	Q_m	k_p
Takahashi et al. [11]	62PMN-38PT	2930	-	-	~90	-
Takahashi et al. [10]	65.25PMN-33.5PT-1.25PMS	~4000	-	-	~300	-
Takahashi et al. [11]	57PMN-38PT-5PMS	2260	-	-	~725	-
Nadoliisky et al. [22]	46PZ*-47PT-7PMS (2 mole Sr doped)	~1600	0.4	-	~1000	~0.420
Aydin [12]	60PMN-30PT-10PMS	~3389	2.2	195	400	0.367
This Study	63PMN-31PT-6PMS	4800	2.5	270	229.7	0.418

*PZ: PbZrO₃

4. Conclusion

In this study, firstly, the physical and electrical properties of PMN-PT-PMS ceramics sintered at 1175 °C for different periods of time were examined. In characterization studies conducted on sintered samples, it was observed that a sintering time of 60 min resulted in lower density values compared to longer periods. The density values obtained for sintering times of 90, 120, and 150 min were around 97.5-98.0%. However, when the sintering time was 150 min, an undesired pyrochlore phase was formed in addition to perovskite structure. The reason for the formation of the pyrochlore phase may be the increase in the volatility of PbO during long sintering time. The fact that the density decreased slightly when sintered for 150 min also supported this idea. XRD analyzes showed that the rhombohedral phase was dominant compared to the tetragonal phase in all samples sintered for different times.

Experimental results revealed that the density, formation of crystalline phases, piezoelectric and dielectric properties of ceramics are sensitive to sintering time. Optimum electrical properties ($d_{33}=270$ pC/N, $K^T=4800$, $k_p=0.418$, $\tan \delta=2.5\%$ and $Q_m=229.7$) were obtained for the samples sintered at 1175 °C for 90 min. This result is a reflection of the high density, low tetragonality and decrease in the amount of pyrochlore phase.

Acknowledgement

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Author's Contributions

Osman Düzen: Drafted the manuscript, performed the experiments and result analyses.

Volkan Kalem: Supervised the experiments' progress, result interpretation and wrote the final manuscript.

Ethics

There are no ethical issues after the publication of this manuscript.

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