Piezoelectric Study of $0.65Pb(Mg_{1/3},Nb_{2/3})O_3$-$0.35PTO_3$ Nanopwoder Ceramics

M. Ghasemifard, S. M. Hosseini, and H. Ghasemifard

***Abstract*—The piezoelectric properties of relaxor ferroelectric $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ ceramic prepared by a sol-gel combustion method have been investigated as function of sintering temperature. The results show that its phase structure is near the morphoteropic phase boundary (MPB), and outstanding electrical properties are obtained with this composition. The highest piezoelectric coefficients were observed for the samples sintered at temperature of 1200°C. In comparison with pure PMN ($(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$--$(x)PbTiO_3$), the substitution of 35% PT results in the decrease of sintered temperature and improved the relaxation behavior.**

***Index Terms*—Dielectric, Gel-combustion, piezoelectric, PMN-PT.**

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1. Introduction

Relaxor ferroelectric PMN-based ceramics such as lead magnesium niobate-lead titanat have been extensively studied for electrostrictive applications including in multilayer capacitors and accurate position actuators due to its high dielectric constant, excellent voltage stability, and low sintering temperature. Mainly, relaxors ferroelectric based on the PMN-PT ($(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$(x)PbTiO_3$) ceramics display excellent piezoelectric/electrostrictive properties along with a variety of compositional modification, because of the volatilization of PbO and the differences of the reactive temperature between Pb-Nb and Pb-Mg[1]-[3], the major problem in synthesis pure PMN-PT ceramics having only a perovskite structure is the formation of pyrochlore phases such as PbO, $Pb_3Nb_4O_{13}$, $Pb_2Nb_2O_7$ and $Pb_5Nb_4O_{15}$. In order to overcome these problems, new preparation and process methods such as Columbite method[3] and molten salt synthesis[4] have been introduced. A successful method is a sol-gel processing[5] which leads to approximately pure perovskite phase at low temperature with an improvement in the properties of PMN-PT ceramics. An additional benefit of this processing is that it leads to small particles size which causes pretty high density of ceramics. We have already managed to prepare PMN-PT nanopowders by sol-gel combustion[6]. This method provides very fine particles and a higher piezoelectric constant compared to traditional mixed oxide processing. Limitation to the employment of PMN-PT in device application has been the lack of a simple, reproducible process for ceramic PMN-PT. Single crystal of PMN-PT with compositions near the MPB have been reported to display very high piezoelectric coefficients (d_{33} > 2500 pC/N), enormously large piezoelectric strains (>1.7%) and very high electromechanical coupling factors (k_{33}>92%). These values are noticeably higher than those provided by the best lead zirconate titanate (PZT) based piezoceramics (600 pC/N to 700 pC/N and 0.17%)[7],[8]. The PMN-PT ceramics have been widely studied in the area of electronic ceramics by many researchers. Alguero *et al.*[9] have been prepared piezoelectric PMN-PT ceramics with 0.2 PT and 0.35 PT from mechanochemically activated powders. The 0.35 PT ceramics offered a first order ferroelectric-paraelectric transition at 171°C and a piezoelectric coefficient of 570 pC/N at room temperature.

The aim of this paper is to investigate the effect of sintering temperature on the properties of 0.65 PMN-0.35 PT ceramics prepared by a new sol-gel combustion processing method. We also have discussed the results of piezoelectric properties for the samples made from PMN-PT as a function of sintering temperature.

2. Experimental Method

Nanopowders of PMN-PT with x=0.35 was synthesized by sol-gel combustion method using metal organic and salts precursors as starting materials. The raw materials used in this experiment include lead nitrate, magnesium acetate and niobium ammonium oxalate and titanium isopropoxide. Aqueous solution of each single cation was prepared; the solutions of lead, titanium, niobium and magnesium were added to the aqueous solution of citric acid under continuous stirring at 65 °C to 70 °C and pH of the sol main-

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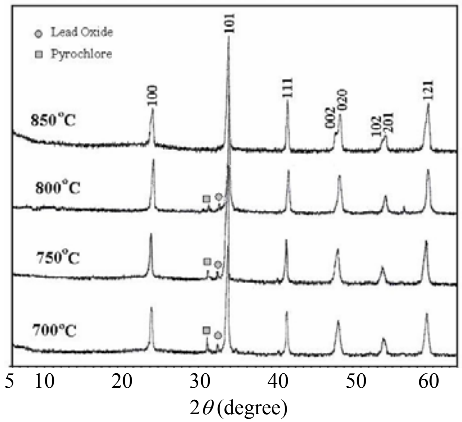


Fig. 1. XRD spectra of samples of the PMN-PT calcinated at different temperatures.

taining at 7 with the addition of ammonium hydroxide. PMN-PT powder was produced by the citrate-nitrate gel auto-combustion technique. More details regarding the synthesis process are described elsewhere[6],[10]. X-ray diffraction patterns of PMN-PT powders (heating rate: 2˚C/min from room temperature to various temperatures ranging from 700˚C to 850˚C for 2 h) are shown in Fig. 1. In this figure we can identify the presence of a monoclinic phase at 850˚C. The XRD results reveal the existence of a perovskite-type phase for gel-combustion method in all temperatures. At temperatures below 850˚C the samples still contain some pyrochlore phases and at 850˚C they completely disappeared.

3. Results and Discussion

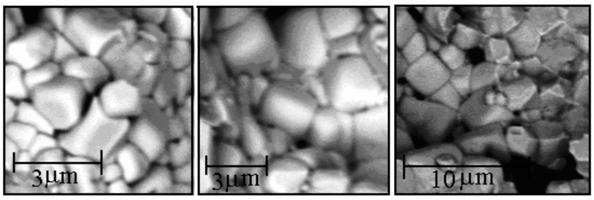
3.1 Microstructure

Fig. 2 shows the microstructure of the PMN-PT ceramics sintered at different temperatures. As can be seen, the grain size increases with sintering temperature.

At sintering temperature of 1200˚C, the grain size of the PMN-PT ceramic is about 1.5 μm, and slowly grows to 2 μm when sintering temperature is increased to 1250˚C. When sintering temperature is further increased to 1300˚C, the grains of the ceramics grow unusually and reach the size to about 3.5 μm. The grain size has strong effects on dielectric properties and polarization of piezoelectric materials[11]. The relationships between the grain size and the ceramics dielectric and piezoelectric properties are discussed in the next section.

3.2 Density

It is really difficult to prepare a well sintered ceramic of Pb($Mg_{1/3}$,$Nb_{2/3}$)O_3 and $PbTiO_3$ by traditional mixed oxides method. Since Pb($Mg_{1/3}$,$Nb_{2/3}$)O_3 structure has an unusually isotropic crystallographic transformation at the Curie temperature (330 ˚C), $PbTiO_3$ shows violent evaporation of PbO.



(a) (b) (c)

Fig. 2. SEM micrographs of surface of PMN-PT ceramics sintered at a) 1200 ˚C, b) 1250 ˚C, and c) 1300 ˚C.

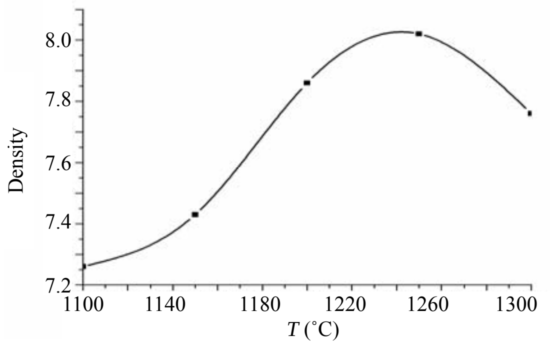


Fig. 3. Density of PMN-PT the ceramics sintered at different temperatures.

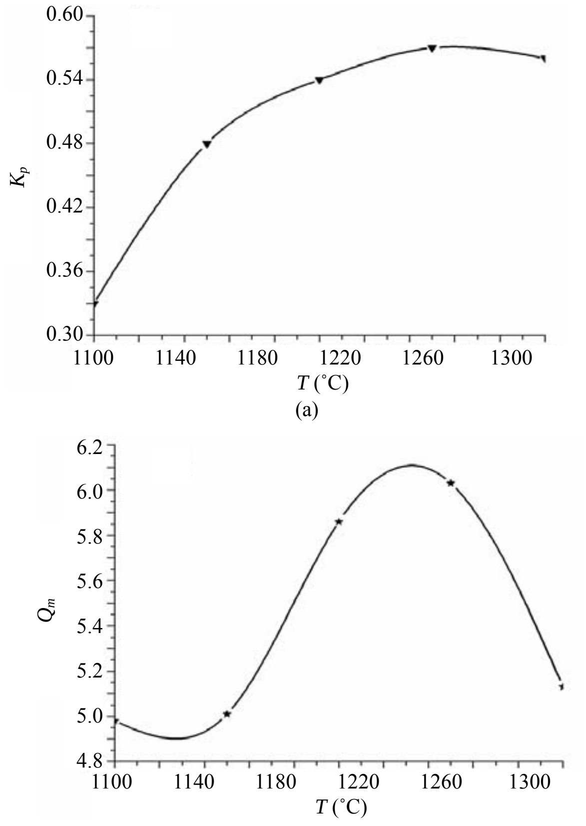
However, the PMN-PT ceramics are free from these difficulties and sintering becomes much easier. All of the compositions are sintered in an air environment at 1100˚C, 1150˚C, 1200˚C, 1250˚C, and 1300˚C for 2 h. In general, the density increases with an raise of temperature until it reaches a maximum peak value at the 1250˚C, then decreases for higher temperature at 1300˚C as shown in Fig. 3. The measured density results are in good agreement with the values reported by Tawfik *et al*.[12]. More details for grain growth of electro-ceramics have been described elsewhere[13],[14].

3.3 Coupling Factor (k_p) and Quality Factor (Q_m)

The electromechanical coupling factor and quality factor are related to different sintering temperature of PMN-PT ceramics as shown in Fig. 4 (a) and Fig. 4 (b). These quantities have been used extensively as a measure of the piezoelectric response of PMN-PT ceramics. They were found that k_p and Q_m depended on the material parameters[15] such as grain size, porosity, and chemical composition. Piezoelectric activity reaches a maximum, when ceramic compositions are chosen near to the morphoteropic phase boundary.

3.4 Dielectric Constant

In piezoelectric ceramics, the properties depend on the composition and crystal structure; the dielectric constant may be increased or decreased through poling action. Fig. 5 shows the dielectric constant *K* of the system. The dielectric constant increases steeply from values of 3000 to 4000 at 1100˚C and 1300˚C, respectively, but decreases to 2500 at 1300˚C.



(a)

(b)

Fig. 4. PMN-PT ceramics characteristics: (a) the electromechanical coupling factor (k_p) and (b) electromechanical quality factor (Q_m).

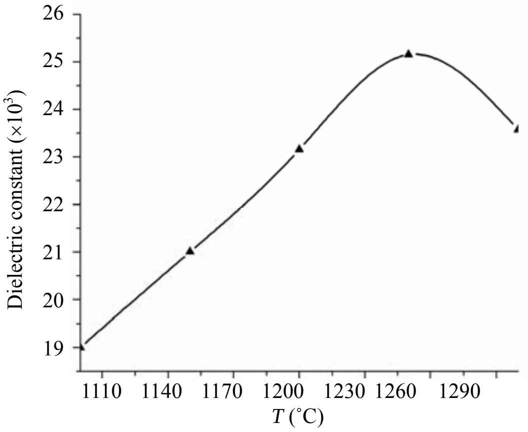


Fig. 5. Dielectric constant of PMN-PT ceramics.

Moreover, the variations of the dielectric constant through poling also rely on the domain alignment and this leads to a rise of dielectric constant. Alignment of domain in large grain size ceramics needs higher field.

3.6 Piezoelectric Coefficient d_{33}

The effective piezoelectric coefficient, d_{33}, for 0.65PMN-0.35PT ceramic at room temperature is shown in Fig. 6. The value of d_{33} reached to a peak value 550 pC/N at 1250°C and drop to 500 pC/N at sintering temperature of 1300°C.

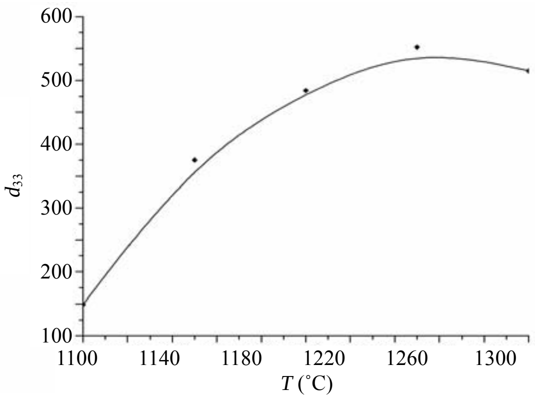


Fig. 6. Piezoelectric coefficient d_{33}, as a function of applied field for PMN-PT ceramics.

Table 1: Some electrical properties for the 0.65PMN-0.35PT ceramics sintered at different temperatures

Tem. (°C)	Grain size (μm)	Density (gr/cm^3)	d_{33} (pC/N)	Q_m	k_p
1100	-	7.26	149	4.98	0.33
1150	-	43.7	375	5.01	0.48
1200	1.5	7.86	484	5.86	0.54
1250	2	8.02	552	6.03	0.57
1300	3.5	7.76	515	5.13	0.56
Ref. [7]	2.8**	7.86	-	-	-
Ref. [8]*	-	-	2200	-	0.92

*PMN-0.32PT single crystal. **Sintering temperature 1240°C.

The electrical parameters of the 0.65 PMN-0.35 PT ceramics prepared from nanopowders and sintered at different temperatures are summarized in Table 1. It seems that the grain size has strong effects on dielectric properties and polarization of piezoelectric materials. The electrical coefficients of PMN-PT reach maximum values when the sample was sintered at temperature 1250°C.

4. Conclusion

The ceramics with the nominal composition of $0.65Pb(Mg_{1/3},Nb_{2/3})O_3$-$0.35PbTiO_3$ were prepared by sol-gel combustion used from unusual precursor. The ceramics samples with dense and uniform microstructure can be obtained at an optimum temperature that lead to increased piezoelectric properties. Electrical properties investigations indicate that excellent ferroelectric and piezoelectric properties were obtained at this composition near the MPB at sintering temperature of 1250°C. This result may be due to grain size growth. In particular, the 0.65 PMN-0.35 PT ceramics of MPB compositions have relativly high piezoelectric properties.

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