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New preparation method of low-temperature sinterable $Pb(Mg_{1/3}Nb_{2/3})O_3$ powder and its dielectric properties

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A relaxor ferroelectric material, $Pb(Mg_{1/3}Nb_{2/3})O_3$(PMN) with perovskite phase was prepared by one-step calcination in the present study. The PMN powder with >99% perovskite phase was prepared successfully by adding an aqueous $Mg(NO_3)_2$ solution rather than MgO to the alcoholic slurry of PbO and Nb_2O_5, followed by calcination at 950°C for 2 h. The DSC and XRD analysis showed that the pathway in the one-step calcination was different from those of the known columbite or solution processes. The PMN powder sintered to 95.6% of the theoretical density at even 900°C for 2 h. Its room temperature dielectric constant showed 13800 at 1 kHz, the loss of dielectric constant of 0.05% and the specific resistivity of 2.4×10^{10} Ω·cm. *© 2000 Kluwer Academic Publishers*

1. Introduction

Lead magnesium niobate (PMN) has applications in multi-layer capacitors and in electrostrictive applications due to its high dielectric constant, excellent voltage stability, and low sintering temperature [1–5]. Basically three methods have been applied to the preparation of PMN dielectrics. One is the conventional mixed oxide method which always gives rise to perovskite PMN with small amount of unwanted cubic pyrochlore $Pb_3Nb_4O_{13}(P_3N_2)$ phase. The other is the mostly used modified oxide method introduced by Swartz and Shrout [6]. It consists of two calcination steps, forming columbite $MgNb_2O_6$(MN) and reacting MN with PbO, which produces the single phase perovskite PMN. The third one is the expensive solution process which resulted in PMN powder with >98% of the perovskite phase. Several modified solution methods have been reported such as through sol-gel [7, 8], citrate gel [9], Pechini route [10], peptization of NbC with H_2O_2 [11], and EDTA gel [12]. Lejeune and Boilot [13] developed low firing (900°C) PMN dielectrics by modifying the mixed oxide method with $MgCO_3$ instead of MgO and adding excess PbO after the calcination step, which exhibited high dielectric constant ($\varepsilon_{max} = 15400$, $\varepsilon_{rt} = 12000$). However, Wang and Schulze [14] reported that in the columbite process with sintering at 1200°C adding excess PbO deteriorate ε_{max} from 13,700 to 6,300, but adding excess 5 wt% MgO improved dielectric constant ($\varepsilon_{max} = 18{,}400$). Goo *et al.* [15] also suggested that excess PbO could not reduce the amount of pyrochlore phase present. The difference in the reports may be attributed to the reactivity of much finer MgO produced from the decomposition of $MgCO_3$ during calcination. Recently Senna *et al.* [16] reported that the single perovskite PMN-PT powder was prepared by reacting basic $Mg(OH)_2$ with acidic Nb_2O_5 in the presence of PbO and TiO_2 via a soft mechanochemical route.

As described above existing preparation methods of the perovskite PMN compound require either two step calcinations or expensive processes. Therefore, efforts were made to develop a simple and economic method by considering the reactivities of the starting materials. Because Nb_2O_5 reacts faster with PbO than MgO to give rise stable cubic pyrochlore P_3N_2, the pure perovskite PMN ceramic can not be obtained by the conventional mixed oxide method. One can postulate that if the reactivities among the constituent compounds can be controlled, the pure perovskite phase can be obtained without the use of the columbite precursor. Since $Mg(NO_3)_2$ is soluble in water as well as in alcohol and a better precursor of MgO than $MgCO_3$, employing $Mg(NO_3)_2$ instead of MgO in a mixed oxide method is expected to go through a different pathway to give the perovskite phase.

In this paper, the authors would like to introduce a new preparation method of the PMN ceramic by one-step calcination from PbO, Nb_2O_5, and $Mg(NO_3)_2$, and then followed by sintering at low temperature.

2. Experimental procedure

The composition of PMN to be synthesized is $Pb(Mg_{1/3}Nb_{2/3})O_3$. Starting materials used in the present study were PbO(99.9%, Aldrich Chem. Co., U.S.A.), Nb_2O_5(99.9%, Aldrich Chem. Co., U.S.A.), and $Mg(NO_3)_2 \cdot 6H_2O$(98%, Fluka Chem. Co., Japan).

In order to compare the reactivities among the starting materials, appropriate mole ratio of the components were prepared by mixing the powder in a mortar or making a slurry in iso-propyl alcohol when $Mg(NO_3)_2$ was used. The mixed powders were subjected to DSC analysis and XRD diffractometry.

Appropriate amounts of PbO (0.15 mol) and Nb_2O_5 (0.1 mol) were placed with iso-propyl alcohol in a polypropylene bottle and milled with zirconia balls ($\varphi = 5$ mm) for 24 h, and then aqueous solution of $Mg(NO_3)_2$(0.105 mol) was added and milled for an additional 2 h. The slurry was rotary evaporated to remove the solvent. About 20 mg of the dried PMN precursor was heated in a Pt/Rh crucible to 1200°C with a heating rate of 10°C/min under a flowing air using TG/DSC (Model 409STA, Netzsch Co., GmbH). Phase developments of the dried powders calcined at various temperatures and times were studied by XRD (Model PW 1800, Philips, NE) between $2\theta = 25$–$35°$ with a scanning rate of 1°/min. The relative amounts of pyrochlore and perovskite phases were determined from the XRD patterns of the heat-treated samples by measuring the major x-ray peak intensities for the perovskite (110) and pyrochlore (222) phases.

The “percentage” of perovskite phase was calculated using the following equation.

$$\%\text{Perovskite} = \frac{\text{Iperov}}{\text{Iperov} + \text{Ipyro}} * 100$$

The powders calcined at 950°C for 2 h showed >99% perovskite phase. The calcined powders were ball milled with 0.5 wt% of PVA 217 in the distilled water for 24 h and then dried by using a rotary evaporator. The dried powder was pressed into pellets at 800 kg/cm^2. They were sintered on a platinum foil in an enclosed alumina crucible at various temperatures for 2 h, i.e. 850°, 900°, 950°, 1100°, and 1200°C. The grain size was determined from SEM (Model S-4200, Hitachi Co., Japan) of the fracture surface of the pellet sintered at 900°C for 2 h. The sintered density was measured by the Archemedian method in water. Dielectric constant and loss of dielectic constant were measured at 1 kHz using Impedance-Gain Phase Analyzer (Model 4194A, Hewlett Packard, U.S.A.). Prior to the dielectric measurements, samples were polished to obtain a flat and parallel surface and electroded with a silver paste by screen printing. Electrical resistivity was measured at room temperature using a picoammeter (Model 4339A, Hewlett Packard, U.S.A.) at 25 V.

3. Results and discussion

Unwanted cubic pyrochlore phase being formed from the reaction between PbO and Nb_2O_5 below 600°C, an approach was pursued to suppress the formation of P_3N_2 and to enhance the reactivity either between Nb_2O_5 and MgO or between PbO and MgO under 600°C.

Comparing the DSC analysis of the mixture of PbO and MgO with that of the mixture of PbO and $Mg(NO_3)_2$ in Fig. 1, PbO reacts with $Mg(NO_3)_2$ to give 5 strong endothermic peaks, but seems to react slowly with MgO to give 3 small endothermic peaks under 800°C.

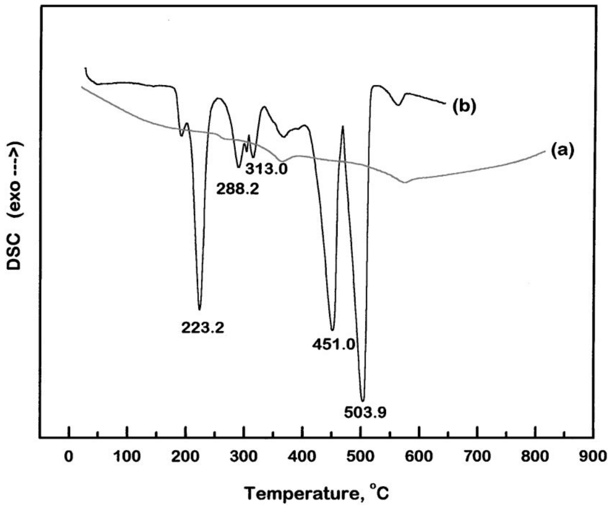

Figure 1 DSC curves of mixture of (a) PbO and MgO and (b) PbO and $Mg(NO_3)_2$ with a heating rate of 10°C/min under a flowing air.

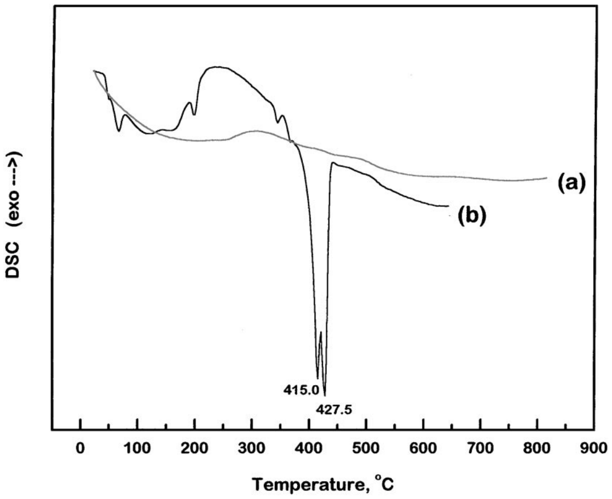

Figure 2 DSC curves of mixture of (a) Nb_2O_5 and MgO and (b) Nb_2O_5 and $Mg(NO_3)_2$ with a heating rate of 10°C/min under a flowing air.

From the DSC curves in Fig. 2 Nb_2O_5 does not react with MgO but reacts with $Mg(NO_3)_2$ to give 2 strong endothermic peaks at 415° and 427°C under 600°C.

From the above DSC analysis it seemed feasible to synthesize the single phase perovskite PMN. Therefore, an attempt was made by introducing less reactive MgO as an aqueous solution of $Mg(NO_3)_2$ to the alcoholic slurry of PbO and Nb_2O_5 so that the Mg^{++} can be distributed uniformly among the reactant oxide particles on atomic scale and also transformed to very fine, reactive MgO upon heating so that it can react with Nb_2O_5 before PbO does. The DSC curve of the PMN precursor shows 5 strong endothermic peaks below 600°C which is similar to that of the mixture of PbO and $Mg(NO_3)_2$ as shown in Fig. 3 and different from that of the PMN precursor prepared by the sol-gel process(an exotherm at 320°C due to decomposition organics present in the gel). The perovskite phase is formed through a columbite intermediate in the Columbite process and amorphous intermediate in the sol-gel process. But the introduced process seems to go through Pb-Mg precursors from analysis of the DSC curves. The pathway is under investigation.

TABLE I Density and dielectric properties of PMN ceramics

Sintering temperature (°C)[a]	Perovskite (%)	Relative density (%)	Dielectric const (ε_{rt}, 1 kHz)	Loss tangent (%)	Resistivity (Ω·cm)
850	100	72.8	5150	0.72	4.8E09
900	100	95.6	13800	0.05	2.4E10
950	100	96.1	13700	0.19	1.2E10
1100	100	97.4	14400	0.39	7.2E10
1200	100	96.4	12900	0.00	2.4E10

[a] Calcined at 950°C for 2 h and sintered for 2 h. Theoretical density of PMN is 8.13 g/cm^3.

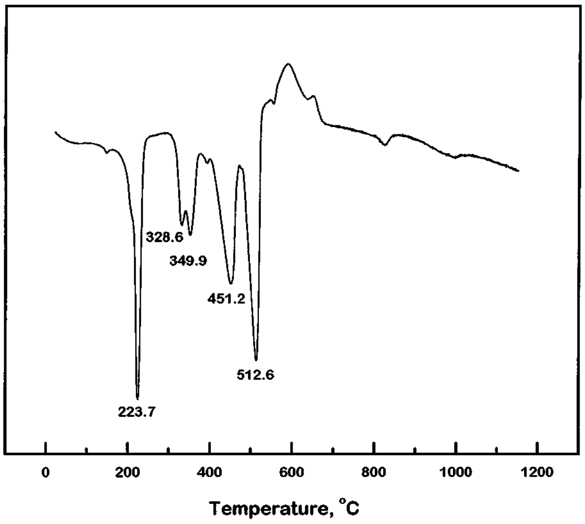

Figure 3 DSC curve of the precursor of PMN prepared from PbO, Nb_2O_5 and $Mg(NO_3)_2$ with a heating rate of 10°C/min under a flowing air.

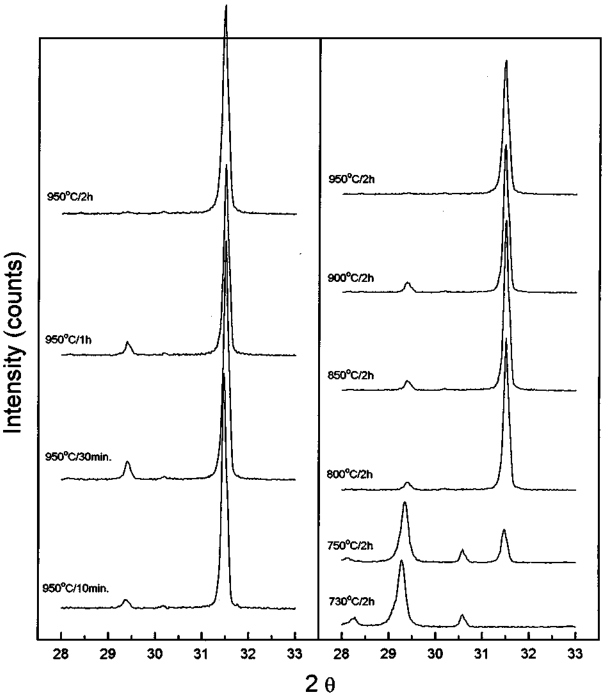

Figure 4 XRD patterns of PMN precursor calcined at different temperatures and times.

With 2 h holding the perovskite phase was formed in 33.7% at 750°C and in 95.4% at 800°C as shown in Fig. 4. The powder calcined at 950°C for 2 h showed 99.3% perovskite phase but holding 10 min at the same temperature gave 96.4% of the perovskite phase. Increasing calcination temperature and time does not seem to affect much on the formation of the perovskite phase unless certain activation energy is fulfilled. From these observations, the formation of the perovskite phase from the pyrochlore phase seems to be kinetically governed.

Calcination was performed at 950°C for 2 h. It consists of two kinds of particles as shown in Fig. 5: one has sizes of 1–1.5 μm and the other 0.2–0.5 μm. What caused the unusual bimodal distribution is not clear. But SEM of the fractured surface of the PMN ceramic sintered at 900°C shows grain size of 2–4 μm as shown in Fig. 6. Although the powder showed bimodal distribution, it sintered relatively homogeneous microstructure without observable abnormal grain growth. Sintered densities and dielectric properties of the PMN ceramics prepared from the powder are shown in Table I.

It is noticeable that the PMN ceramic with the perovskite single phase can be prepared by sintering at 900°C for 2 h with excellent properties, i.e. 13800 of room temperature dielectric constant, 0.05% of dielectric loss at 1 kHz, and 2.4×10^{10} Ω·cm of specific resistivity. Increasing sintering temperature did not affect on the dielectric properties significantly but increased the relative density from 96% to 98%.

The general characteristics of various PMN ceramics that were sintered at 900°C in this study and reported in other works are compared in Table II. The ε_{rt} value of 13800 in this study at 1 kHz is higher than those of previous reports. The sintering condition of 900°C for 2 h is also favorable than the others. It can be fired with 70%Ag-30%Pd internal electrodes in multilayer ceramic capacitors. The bimodal size seemed to be attributed to grain growth even at 900°C, submicron sized PMN powder obtained from the sol-gel process did not sinter at 900°C and grains were smaller than 1 μm.

As described in this paper the perovskite single phase PMN ceramic can be prepared successfully by modifying the conventional mixed oxide process, i.e. replacing the least reactive oxide component with a reactive form. Such prepared PMN powder, for an example, sinters at 900°C, lower than that of the sol-gel process by 300°C. Futhermore it showed even better dielectric properties than those prepared by the sol-gel and the mixed oxide processes. This new process is reproducible, simple, economic and can employ cheaper chemicals.

It opens the possibility to apply the introduced process to synthesis of PbO-based complex perovskite compounds as well as to modify known processes with reactivities among components.

TABLE II Comparison of general characteristics of various PMN ceramics

Sample from	Processing	Calcination temp., time	Sintering temp., time	ρ_{rel} (%)	1 kHz		Grain size (μm)
					ε_{max}	ε_{rt}	
Roy *et al.*	Sol-gel	950, 2	900, 4	~90	3000	2700	<1.0
			1250, 4	97.6	15900	11700	5–8
Schulze *et al.*	Columbite	1000, 6 & 800, 4	1200, 1	98.0	18400		1.4–3.8
Boilot *et al.*	Mixed oxide with $MgCO_3$	800, 2	900, 6	96	15400	12000	
This work	Mixed oxide with $Mg(NO_3)_2$	950, 2	900, 2	95.6	n.a.	13800	2–4

n.a.: not available.

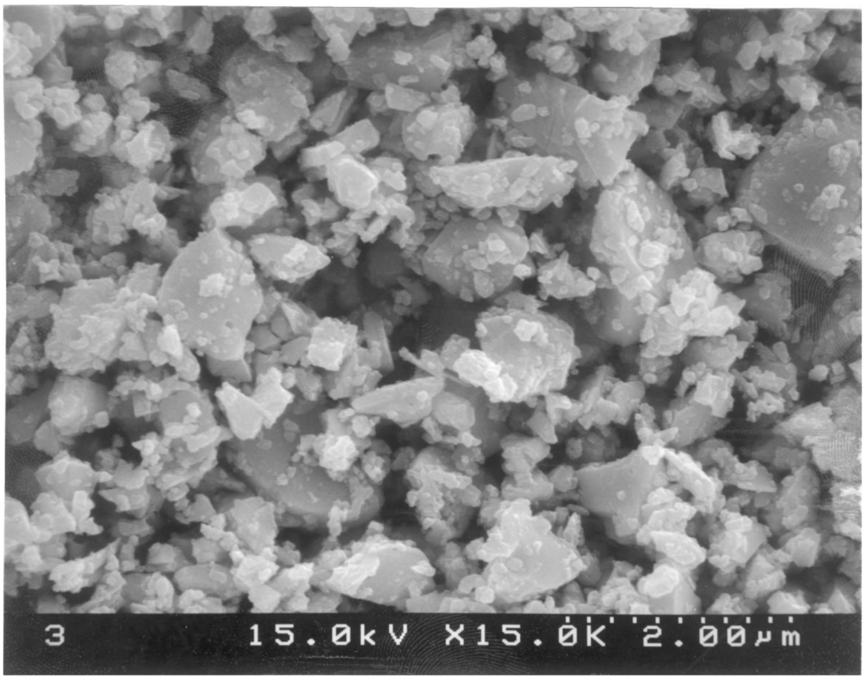

Figure 5 SEM micrograph of PMN powder calcined at 950°C for 2 h.

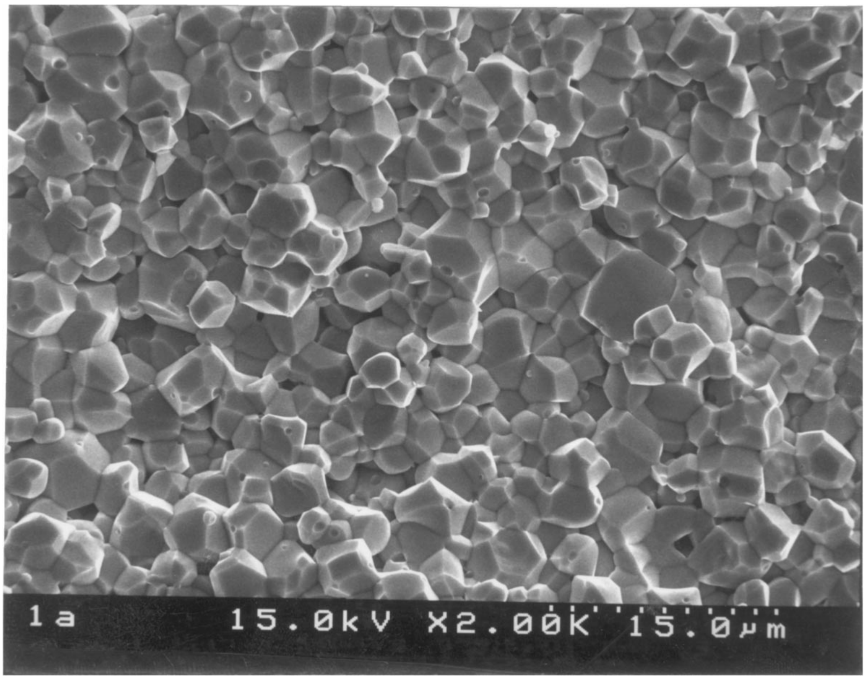

Figure 6 SEM micrograph of fractured surface of PMN ceramic sintered at 900°C for 2 h.

4. Conclusion

A new process has been developed for the preparation of PMN powder with >99% perovskite phase by one-step calcination.

The PMN powder with the perovskite single phase was obtained by adding an aqueous solution of $Mg(NO_3)_2$ to the alcoholic slurry of PbO and Nb_2O_5, followed by calcination at 950°C for 2 h. Such prepared PMN powder sintered greater than 96% of the theoretical density at 900°C for 2 h which is low sintering temperature for the PMN ceramics at which it can be fired with 70%Ag-30%Pd. It showed a room temperature dielectric constant of 13800, a loss of dielectric constant 0.05% at 1 kHz, and a specific resistivity of 2.4×10^{10} Ω·cm.

References

1. T. R. SHROUT and A. HALLIYAL, *Am. Ceram. Soc. Bull.* **66** (1987) 704.
2. Y. HAKATANI *et al.*, U.S. Pat. 5,004,715 (1991).
3. S. NOMURA and K. UCHINO, *Ferroelectrics* **50** (1983) 19.
4. K. UCHINO, *Am. Ceram. Soc. Bull.* **65** (1986) 647.
5. C. E. WHEELER and B. G. PAZOL, *ibid.* **70** (1991) 117.
6. S. L. SWARTZ and T. R. SHROUT, *Mater. Res. Bull.* **17** (1982) 1245.
7. P. RAVINDRANATHAN, S. KOMARENI, A. S. BHALLA and R. ROY, *Ferroelectrics Lett.* **11** (1990) 137.
8. F. CHAPUT, J. P. BOILOT, M. LEJEUNE, R. PAPIERNIK and L. G. HUBERTPFALZGRAF, *J. Am. Ceram. Soc.* **72** (1989) 1355.
9. J.-H. CHOY, J.-S. KANG, S.-T. HONG and D.-G. KIM, *Mater. Res. Bull.* **25** (1990) 283.
10. H. U. ANDERSON, M. J. PENNELL and J. P. GUHA, in “Ceramic Powder Science I” (The American Ceramic Society Inc., Ohio, 1987) p. 91.
11. J. P. LEE, J. LEE, S. KANG and H. KIM, *J. Korean Ceram. Soc.* **33** (1996) 17.
12. Y. NARENDAR and G. L. MESSING, *J. Am. Ceram. Soc.* **80** (1997) 915.
13. M. LEJEUNE and J. P. BOILOT, *Am. Ceram. Soc. Bull.* **64** (1985) 679.
14. H.-C. WANG and W. A. SCHULZE, *J. Am. Ceram. Soc.* **73** (1990) 825.
15. E. GOO, T. YAMAMOTO and K. OKAZAKI, *ibid.* **69** (1986) C188.
16. J.-G. BAEK, T. ISOBE and M. SENNA, *ibid.* **80** (1997) 973.

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