

Preparation of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Powder using a Citrate-Gel Derived Columbite MgNb_2O_6 Precursor and its Dielectric Properties

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Abstract

A (Mg,Nb)-citrate gel has been prepared by the solvent evaporation of mixed solution, which was made by dissolving $\text{Mg}(\text{NO}_3)_2$, NbCl_5 , and citric acid, and subsequently fired in the temperature range of $650\sim 950^\circ\text{C}$ to yield columbite-phase MgNb_2O_6 precursor. The obtained citrate gel and the fired powders were characterized by TG/DT analysis, FT-IR spectrophotometer, XRD, particle size analyzer, and SEM. X-ray diffraction analysis indicated that the columbite-phase MgNb_2O_6 precursor was formed with the minor phases of Nb_2O_5 and $\text{Mg}_4\text{Nb}_2\text{O}_9$ when the citrate gel was heat-treated. The citrate-gel derived columbite MgNb_2O_6 precursor was a finer and more reactive powder than that obtained by solid-state reaction as evidenced by its ability to react with PbO . The percent of perovskite-phase $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ in the calcined powders increased as the calcination temperature increased. $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics fabricated from citrate-gel derived columbite MgNb_2O_6 precursor could be highly sintered at ca 850°C . The maximum dielectric constant of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics was found to increase with the sintering temperature. The grain size dependence of dielectric constant can be explained as a consequence of low-permittivity grain boundaries. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Lead magnesium niobate, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), is an important relaxor ferroelectric material with a perovskite structure. The excellent dielectric and electrostrictive properties make it a

useful material for multilayer ceramic capacitor and electrostrictive actuator applications.^{1,2} Therefore, there has been a great deal of interest in the preparation of single-phase PMN powder. It is very difficult, however, to synthesize single-phase PMN by the solid-state reaction of the constituent oxides due to the low dispersion of MgO .^{3,4} The conventional mixed oxide method frequently leads to the appearance of (Pb,Nb,O)-based pyrochlore phases. The conversion of the pyrochlore phases into perovskite phase is difficult even by firing for prolonged periods at an elevated temperature. Recently, we have prepared fine (1-x)PMN-x $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ powders using the molten salt synthesis.⁵

In 1982, Swartz and Shrout proposed the columbite precursor method. In the method, an intermediate step to give columbite MgNb_2O_6 precursor is used to bypass the formation of the pyrochlore phases.⁶ Similarly, Guha and Anderson examined the effect of the cubic pyrochlore phase, $\text{Pb}_3\text{Nb}_2\text{O}_8$.⁷ Horowitz *et al.*⁸ and Saha *et al.*⁹ used the modified columbite precursor methods to obtain highly reactive powders. Kakegawa *et al.* also applied the two-step method to obtain $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ powder using organic chelating agent, oxine.¹⁰ More recently, Gupta *et al.* developed the partial oxalate route to improve the mixing and the reactivity of PMN powder.¹¹

The perovskite-type oxides have been extensively synthesized over 100 different mixed-metal oxide system by Pechini method.^{12–14} For the synthesis of PMN powders, Choy *et al.* adopted a modified Pechini method used chelating ability of citric acid.¹⁵ However, the preparation of columbite MgNb_2O_6 precursor using citric acid and its effect on the formation of PMN have not been adequately characterized. This two-step method for the preparation of PMN has the advantage that only B site cations are required to be precipitated

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simultaneously and, thereby, the precipitation of lead chloride can be bypassed.

In this study, the main objectives are (a) the development of citrate-gel derived columbite precursor method for the preparation of highly reactive precursor powder, (b) the determination of the processing conditions to obtain a single-phase perovskite PMN powder, and (c) the investigation of dielectric properties of PMN ceramics fabricated from this PMN powder.

2 Experimental Procedure

The citrate gel has been prepared as follows; at first, magnesium nitrate (0.0255 mol) was dissolved in citric acid solution (0.1125 mol), and 20 ml of 30% hydrogen peroxide solution was added to magnesium–citric acid solution. Then, niobium chloride (0.0500 mol) was mixed together. At this stage, the pH of the mixed solution was ca 1.5 and was adjusted up to 6.5 by adding 6 N NH₄OH solution.^{15,16} It is the optimum pH condition for the homogenous metal complex solution. The resulting clear solution was heated at 70~75°C while it was mechanically stirred. After the water evaporated, the solution was turned into a pale-yellow gel with high viscosity. The citrate gel was fired in the temperature range of 650 to 950°C under flowing O₂ gas. To compare with citrate-gel derived columbite precursor method (CG–MNP method), the columbite precursor was also prepared by the conventional columbite precursor method (C–MNP method). Reagent-grade MgO and Nb₂O₅ were ball-milled in ethanol for 24 h and calcined at 1000°C for 4 h.

The precursor powders obtained from the two methods were mixed with PbO for 24 h and calcined at 600, 700, and 800°C for 2 h. The powders calcined at 800°C were mixed with 3 wt% polyvinyl alcohol as a binder, and dried in an oven at 110°C. The dried powders were ground by mortar and pestle, pelletized into disks, and then sintered in a double inverted Pt crucible. To minimize the PbO loss, the pellets were covered with the PMN powder obtained from C–MNP method. For capacitance measurement, the pellets were polished by SiC paper and electroded with silver paste at 650°C. The density of the sintered bodies was measured by the Archimedes method. The temperature dependence of the capacitance was determined whilst cooling the sample.

The thermal behavior of the citrate gel was studied by means of thermogravimetric and differential thermal analysis (TG/DTA, Stanton Redcroft TGA-1000) at heating rates of 10°C min⁻¹ and FT-infrared spectrophotometer (FT-IR, BOMEM

MB-102). The phases of samples were identified by X-ray diffractometry (XRD, Rigaku D-MAX III-b) using CuK_α radiation. The relative amount of perovskite-phase PMN against the pyrochlore phase was calculated from the relative intensities of the major X-ray reflections for the perovskite and pyrochlore phases peak as given by the equation: % perovskite = [I_{perov (110)} / (I_{perov (110)} + I_{pyro(222)})] × 100, where I_{perov(110)} and I_{pyro(222)} refer to the (110) perovskite and (222) pyrochlore peak, respectively. The distribution of particle size was measured by a laser particle size analyzer (Granulometer HR 850, Cilas-Alcatel). The microstructures of the fractured surface were examined by scanning electron microscopy (SEM, JEOL JSM 840 A) equipped with energy-dispersive X-ray spectroscopy (EDS). The capacitance and dissipation factor were measured by LCR meter (Kokyo KC-536) at 1 kHz.

3 Results and Discussion

3.1 Preparation of columbite MgNb₂O₆ precursor

The preparation of a homogeneous gel is the most crucial step in the CG–MNP method. To achieve this, the pH of the mixed metal solution was kept at 6.5 during the evaporation of the water.^{15,16} The hydrogen peroxide solution having high negative electric potential, -1.77, was used to stabilize the niobium species existing as peroxy complex ions in solution.¹⁷ The obtained citrate gel is presumed to be an intimate mixture of citrates and nitrates. Elemental analysis of the citrate gel by inductively coupled plasma-atomic emission spectrometry (ICP–AES) gave the following; Mg:Nb = 7.95: 58.4 ppm in agreement with the starting composition within the experimental error.

To find an optimum firing temperature of the citrate gel, thermogravimetric and differential thermal analyses were conducted and illustrated in Fig. 1. Endotherm below 100°C is originated from the removal of the residual solvents. The abrupt mass decrease above 200°C, which corresponds to an endothermic DTA peak, may be attributed to the thermal decarboxylation of citric acid.¹⁸ The decomposition goes on further to give exothermic behaviors at 520 and 590°C, which might be due to the decomposition of intermediate and the crystallization of columbite phase, respectively.¹⁵ The weight loss between room temperature and 650°C for the citrate gel is found to be 84%. According to TG/DTA of the citrate gel, the minimum firing temperature to get organic-free columbite MgNb₂O₆ precursor is ca 650°C.

The formation of metal–citrate complex was monitored by FT–IR spectrum of the citrate gel as

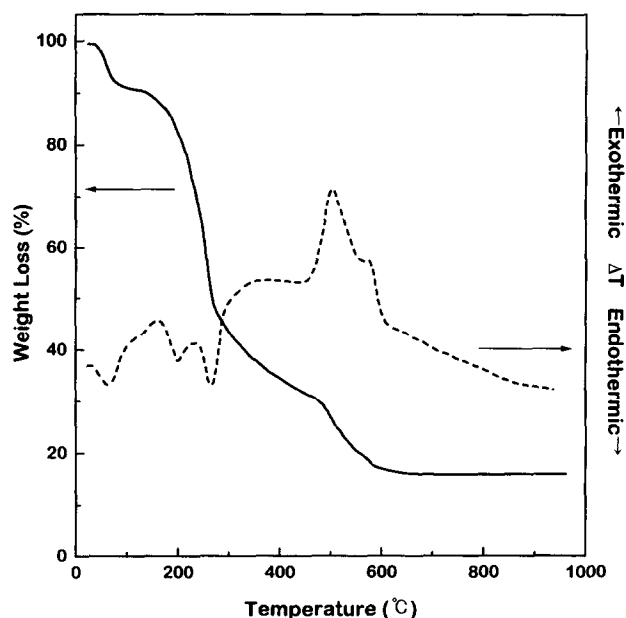


Fig. 1. TG/DTA of the citrate gel at a heating rate $10^{\circ}\text{C min}^{-1}$ (-TG, ... DTA).

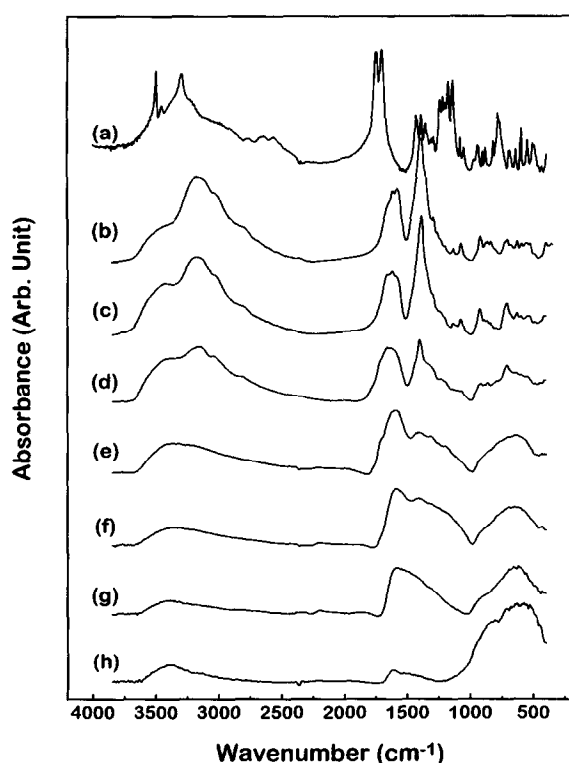


Fig. 2. FT-IR spectra of CG-MNP fired at various temperatures. (a) Citric acid, (b) the citrate gel, (c) 200°C , (d) 300°C , (e) 400°C , (f) 500°C , (g) 600°C , and (h) 650°C .

shown in Fig. 2(b). The carboxylate group coordinated to metal gave rise to asymmetric (ν_{as}) and symmetric (ν_{s}) stretching bands at 1600 and 1406 cm^{-1} , respectively, whereas the free carboxylic acid showed a typical absorption band at $1735\sim 1705\text{ cm}^{-1}$.¹⁸ Both carboxylate and carbonate bands also appeared at 1595 and 1418 cm^{-1} , respectively. The large metal oxide band was observed at $850\sim 400\text{ cm}^{-1}$. At 650°C , both carboxylate and carbonate bands were decreased

whereas the metal oxide band was increased, which agrees with the result of TG/DTA.

Figure 3 shows the powder XRD patterns of CG-MNP powders obtained by the firing of the citrate gel in the temperature range of $650\sim 950^{\circ}\text{C}$. The powders fired at 650 and 750°C consisted of the mixed phases of disordered columbite MgNb_2O_6 , Nb_2O_5 (JCPDS 27-1003), and unknown phase. As the firing temperature is elevated to 850°C , the amount of ordered phase columbite (JCPDS 33-0875, $a = 0.5711$, $b = 1.4206$, and $c = 0.5045\text{ nm}$) resulted from 1:2 ordering is increased. However, $\text{Mg}_4\text{Nb}_2\text{O}_9$ (JCPDS 36-1381) and Nb_2O_5 (JCPDS 27-1311) are also increased as the firing temperature increases above 900°C . These results disagree with Goldschmidt's work on phase equilibria in Mg-Nb-O system. Goldschmidt reported that columbite MgNb_2O_6 prepared by mixed oxide method was the thermodynamically stable phase below 1400°C . This difference observed in CG-MNP method may be ascribed as the difference of the phase stability for CG-MNP or a variation of the cation stoichiometry. Although we have not completely understood yet the reason for the instability of columbite MgNb_2O_6 phase above 900°C , we can suggest that the optimum firing temperature for the preparation of columbite MgNb_2O_6 precursor is around 850°C .

3.2 Synthesis of perovskite PMN

Figure 4 shows the XRD patterns of PMN powders which were obtained from the reaction

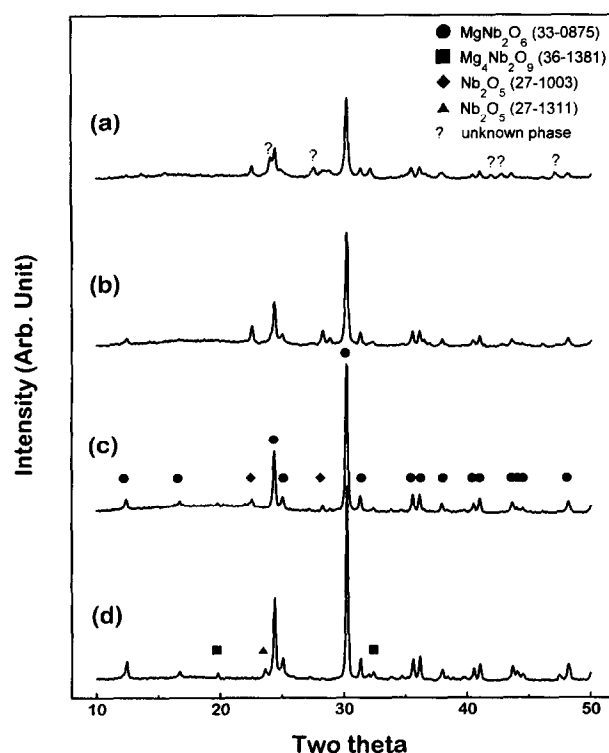


Fig. 3. Powder XRD patterns of CG-MNP fired at various temperatures. (a) 650°C , (b) 750°C , (c) 850°C , and (d) 950°C .

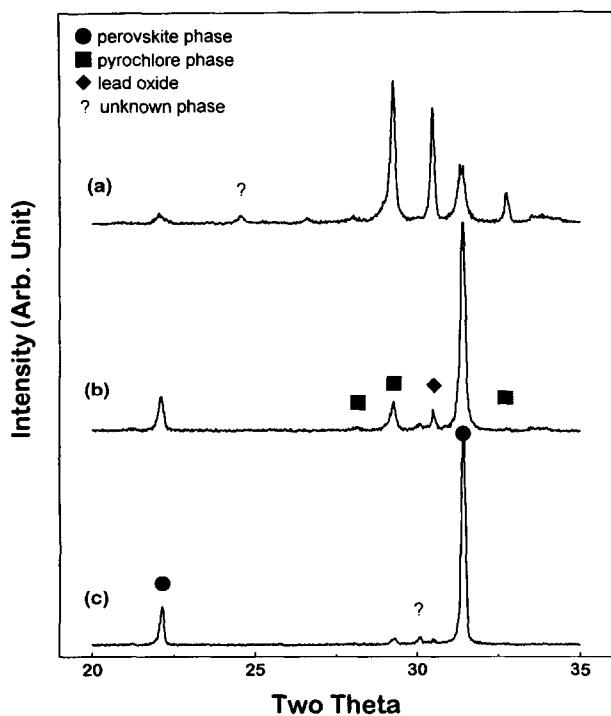
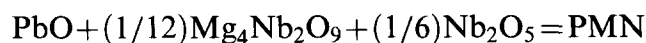


Fig. 4. Powder XRD patterns of PMN powder obtained from CG-MNP at various temperatures. (a) 600°C, (b) 700°C, and (c) 800°C.

between PbO and CG-MNP. As the calcination temperature increases, the amount of perovskite PMN is increased with corresponding to the decrease in pyrochlore phase. The cubic pyrochlore phase coexists with perovskite phase at lower calcination temperature and nearly transforms into the perovskite phase at 800°C. According to the earlier study, the three pyrochlore phases, such as cubic $\text{Pb}_3\text{Nb}_4\text{O}_{13}$, rhombohedral $\text{Pb}_2\text{Nb}_2\text{O}_7$ and $\text{Pb}_5\text{Nb}_4\text{O}_{15}$, and tetragonal $\text{Pb}_3\text{Nb}_2\text{O}_8$, can be formed as reaction intermediates in the temperature range of 500~700°C. Above 700°C, the pyrochlore phases reacted with MgO to give the cubic perovskite PMN.^{19,20} The pyrochlore phases is, however, not completely eliminated. Table 1 shows the percent of perovskite phase for PMN powders prepared from CG-MNP powders. Although the firing temperature of the citrate gel is quite different, the percent of perovskite phase exhibits very similar change in every cases. This result might indicate that the minor phases of Nb_2O_5 and $\text{Mg}_4\text{Nb}_2\text{O}_9$ also participate in the reaction with PbO to form perovskite PMN as follows:

Table 1. The percents of the perovskite PMN phase prepared from the reaction between PbO and CG-MNP powder

Reaction temperature with PbO (°C)	Firing temperature of the citrate gel (°C)			
	650	750	850	950
600	34.6	37.0	34.0	34.1
700	89.1	85.0	88.7	86.0
800	94.9	98.0	97.9	96.3



That is, the formation of perovskite phase is not greatly affected by the firing temperature of the citrate gel even though CG-MNP powders are consisted of the mixed phases.

3.3 Comparison between CG-MNP and C-MNP method

Figure 5 shows the morphologies of MN precursors and PMN powders prepared from CG-MNP and C-MNP methods. Although CG-MNP calcined at 850°C is agglomerated, the powder is very small and fluffy-like powder. On the other hand, C-MNP shows partially overgrown particle. Figure 6 shows the particle size distribution morphologies of MN precursors and PMN powders prepared from CG-MNP and C-MNP methods. At a glance, the median particle size of CG-MNP (5.09 μm) is larger than that of C-MNP (4.11 μm). After ball milling for 2 h, however, the median particle size of precursors is reduced to 0.53 and 0.64 μm , respectively. This fact explains why the synthesis of perovskite PMN using CG-MNP method is more facile than that by C-MNP method. That is, the cohesive power of CG-MNP is weak and the agglomerated precursor can be fully segregated into small particles in mixing step with PbO. The small particle size of CG-MNP enables the formation of fine PMN powder due to the short reaction path, thereby facilitating subsequent sintering operations.

According to the XRD result of PMN ceramics sintered at 1000°C, the percent of perovskite PMN is over 99% for CG-MNP method, whereas ca 93% for C-MNP method. Therefore, the CG-MNP method is much better than C-MNP method in preparing perovskite PMN powder. The elemental analyses by energy-dispersive X-ray spectroscopy are listed in Table 2. The chemical composition of PMN ceramics fabricated by both methods is in agreement within the instrumental error.

3.4 Dielectric properties and microstructure of PMN ceramics

The change in density versus the sintering temperature is given in Fig. 7. As is evident from the Fig. 7, rapid densification in PMN ceramics fabricated from CG-MNP method occurred at 825°C and subsequently reached a theoretical density of 98% at 850°C. Further increase in the sintering temperature causes a slight decrease in the density values. According to Horowitz, for PMN ceramics

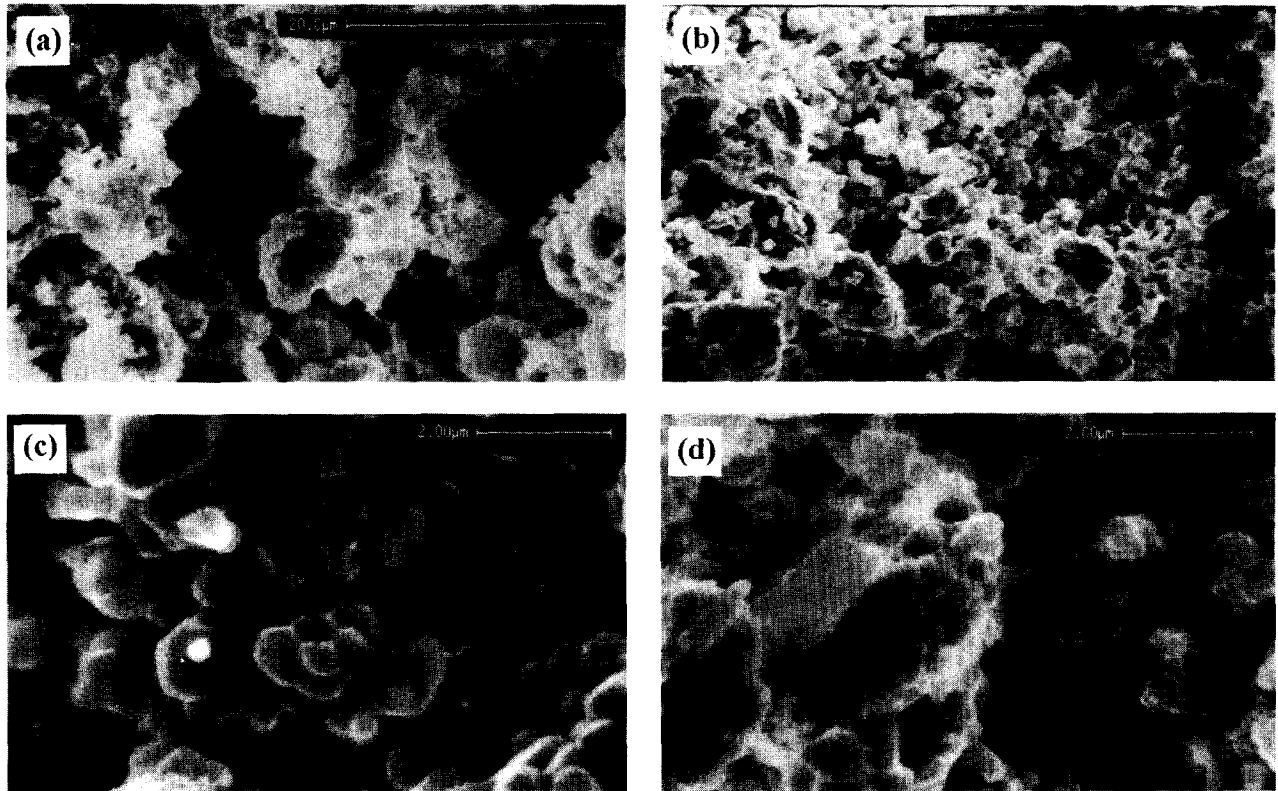


Fig. 5. SEM photographs of (a) CG-MNP fired at 850°C, (b) C-MNP fired at 1000°C, and PMN obtained from (c) CG-MNP and (d) C-MNP.

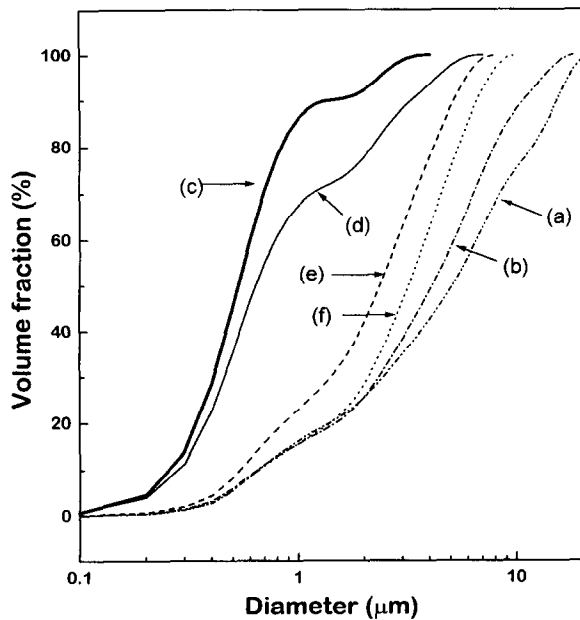


Fig. 6. Particle size distributions of (a) CG-MNP fired at 850°C, (b) C-MNP fired at 1000°C, (c) ball-milled CG-MNP, (d) ball-milled C-MNP, and PMN powder obtained from (e) CG-MNP and (f) C-MNP method.

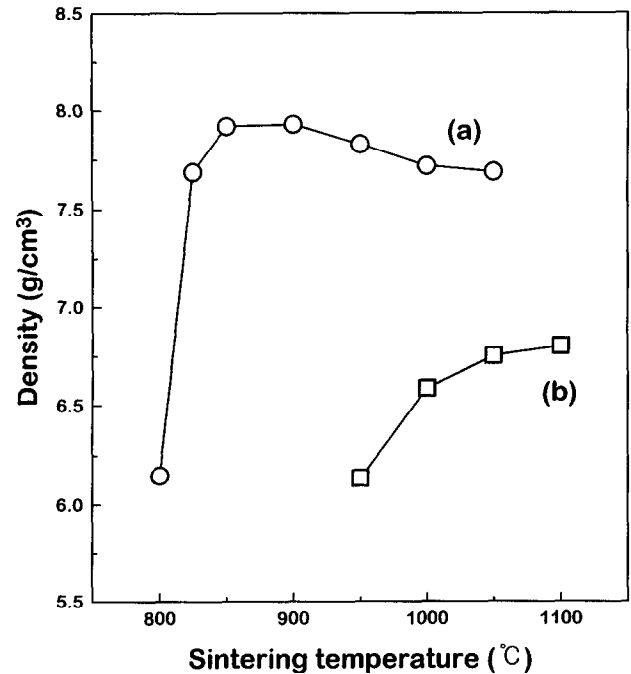


Fig. 7. Density versus sintering temperature of PMN ceramics obtained from (a) CG-MNP and (b) C-MNP method.

Table 2. The elemental analysis of PMN ceramics fabricated from CG-MNP and C-MNP method and sintered at 1000°C

Element	CG-MNP method	C-MNP method	Calculated value (wt%)
Pb	19.4	19.9	20.0
Mg	6.1	6.3	6.7
Nb	13.9	13.6	13.3

derived by acetate and oxalate solution, high density could not be achieved because of the agglomerate nature of the precursor.⁸ In CG-MNP method, only a very low sintering temperature is required to densify PMN ceramics and the sintering temperature that yielded the highest density is in the temperature range of 850~900°C. This result

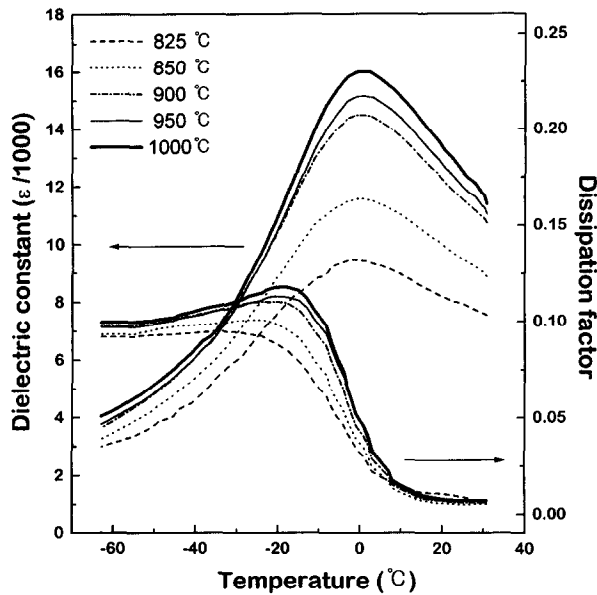


Fig. 8. Dielectric constant and dissipation factor of PMN ceramics obtained from CG-MNP.

may be explained in terms of the smaller particle size of PMN powder obtained from CG-MNP method ($2.37 \mu\text{m}$) as shown in Fig. 6. Above this temperature, the densification process is strongly influenced by PbO volatilization.²¹ The result in Fig. 7 seems to be a compromise between densification and PbO loss. However, PMN ceramics derived by C-MNP method exhibit a low density due to the partly overgrown particle in PMN powder and the incomplete transformation of pyrochlore phase into perovskite phase. Even at sin-

tering temperature of 1100°C , the obtained body has a low relative density of 82%. The high density at relatively low sintering temperature indicates the advantage of the CG-MNP method over the C-MNP method.

The variation of dielectric constant and dissipation factor as a function of temperature for the PMN ceramics are shown in Fig. 8. It can be seen that PMN ceramics display diffuse phase transition behavior typical of relaxors. The maximum dielectric constant increases from 9200 to 15800 as the sintering temperature increases from 825 to 1000°C , whereas that of PMN ceramics fabricated by C-MNP is low. In general, the dielectric constant is largely dependent on the presence of the pyrochlore phases, the degree of sintering, and the grain size. In this study, the amount of pyrochlore phase is not changed above 825°C and the density is decreased above 900°C . As shown in Fig. 9, however, the grain size of the PMN ceramics increase as the sintering temperature increases. A grain size variation from 1.3 to $5 \mu\text{m}$ can be seen for the ceramics sintered from 850 to 1000°C .

The most apparent result is that the dielectric constant of the PMN ceramics is dependent on the grain size. There are many reports related to the dependence on dielectric constant on the grain size.^{8,22,23} This dielectric dependence can be discussed in detail considering (1) co-operative microdipole-dipole interaction between superparaelectric regions and (2) a low polarizable phase boundary.¹¹ The grain-size dependence is mainly

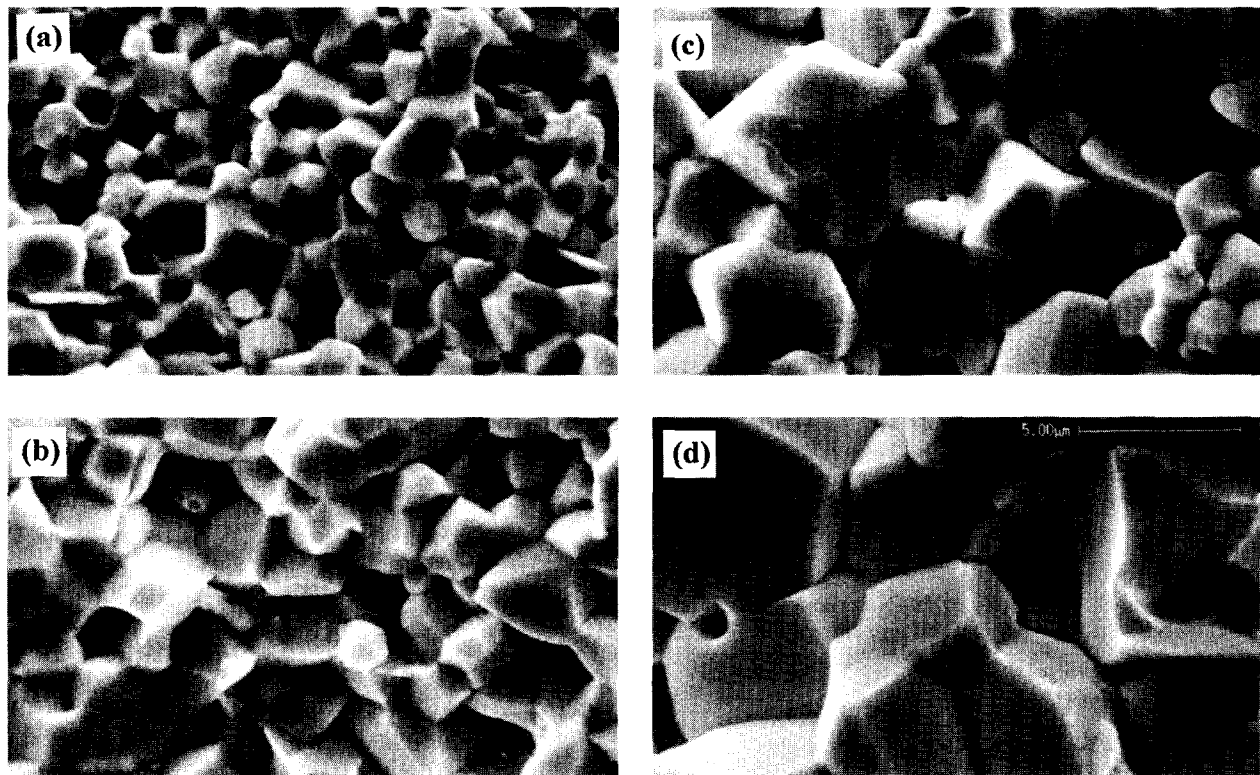


Fig. 9. SEM photographs of PMN ceramics sintered at various temperatures. (a) 850°C , (b) 900°C , (c) 950°C , and (d) 1000°C .

caused by the grain boundary volume. Swartz *et al.* postulated that amorphous PbO and impurities exist along the grain boundaries. This may be the reason for the reduction of dielectric constant when the grain size is small. In other words, as the grain size is increased, the number of grain boundaries is decreased and the large permittivity of the PMN grains becomes less affected by the low permittivity grain boundaries.²³ In addition, dielectric loss, originated from resistivity of the dielectric, porosity, and grain boundaries, is increased with the dielectric constant.

4 Conclusions

Among the two methods, we have shown that the CG-MNP method is a better method for suppressing the formation of pyrochlore phases and enhancing the sinterability of PMN ceramics. The CG-MNP method gives the homogeneous mixing of the corresponding metals in solution, which can lead to the formation of fine precursor powder. The pyrochlore phase is observed as reaction intermediates and transforms into the perovskite phase as the calcination temperature increases. The particle size of the precursor and PMN powder obtained from CG-MNP method is smaller than that of C-MNP method. The most important result in this study is the sintering temperature that yielded the highest density is 850~900°C. This is very useful for the use of Ag-Pd internal electrodes. Microstructure analysis revealed that the grain size controlled the dielectric properties and appeared to be more dominant factor on dielectric properties.

Acknowledgement

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