Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1485–1488

www.elsevier.com/locate/jeurceramsoc

# Effects of depressor addition on electrical properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ dielectric ceramics

M. Kobune[a,*], K. Yamakawa[a], T. Yamashiki[b], T. Akamatsu[b]

[a]Graduate School of Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji 671-2201, Japan
[b]Electronic & Imaging Res. Labs., Toray Industries, Inc., 1-2, Sonoyama 3-chome, Otsu, Shiga 520-0842, Japan

## Abstract

To develop inorganic dielectric materials for layer insulating materials with high dielectric constant and low dielectric loss of next-generation system-in-a-package, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) and PMNT-$Pb(Mg_{1/2}W_{1/2})O_3$–$Pb(Fe_{1/2}$ $Ta_{1/2})O_3$ (PMNT–PMW–PFT; PMNT–PMWFT) ceramics were fabricated by the columbite precursor method. The addition of 1.0 mass% excess MgO to PMNT 94/6 was effective in restraining the formation of the pyrochlore phase and stabilizing the perovskite phase. When the mixing proportion (mol%) of PMNT 94/6/PMWFT 85/15 was 80/20, good dielectric properties with relative permittivity, $\varepsilon_r$ of 4660 and dielectric loss, tan$\delta$ of 0.06% at 1 MHz were obtained. By varying the mixing proportion of PMW/PFT in PMWFT, which plays an important role of depressor to PMNT, 0.8PMNT 94/6·0.2PMWFT 70/30 ceramics having high $\varepsilon_r$ of 5810, low tan$\delta$ of 0.07% at 1 MHz and their flat frequency characteristics were obtained by means of the effects of depressor addition to PMNT.
© 2003 Elsevier Ltd. All rights reserved.

*Keywords:* Depressor; Dielectric properties; Perovskites; PMNT; PMWFT

## 1. Introduction

Recently, system-in-a-package (SIP), which consists of passive parts, a layer insulating material with low dielectric constant, signal circuits, connecting circuits and a layer insulating material with high dielectric constant, and supports the implementation of a next-generation high speed semiconductor has attracted much attention as a promising system for intelligent transport system (ITS)[1] applications with system-large scale integrated circuit (system LSI). To build up the above SIP, there are several technical problems to be solved. Particularly, the improvement in transmission characteristics of insulating materials has been strongly required to realize the large-capacity high speed signal processing. To solve this problem, we think that the development of inorganic dielectric materials maintaining the high frequency properties of high relative permittivity, $\varepsilon_r$ of more than 1000 at 1 MHz and low dielectric loss, tan$\delta$ of less than 0.1% at 1 MHz is essential. For these requirements, relaxor-ferroelectrics which are generally expressed by $Pb(B_1, B_2)O_3$ with high $\varepsilon_r$ and relatively small temperature coefficient appear to be potential dielectric materials. Especially, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) with perovskite structure, which was discovered by Smolensky et al.[2] in the latter half of the 1950s can be characterized by the flat temperature characteristic of $\varepsilon_r$ in the vicinity of R.T. and low temperature sintering. Ogasawara and Mito[3] took notice of the attractive characteristics of PMN described above and previously revealed that the formation of pyrochlore phase could be restrained by adding 10–15 mass% MgO to $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Mg_{1/2}W_{1/2})O_3$–$PbTiO_3$ (PMN–PMW–PT; PMNWT), resulting in an acquisition of high $\varepsilon_r$. However, as tan$\delta$ (=0.5%) of the above PMNWT 1/54/45 materials[3] with high $\varepsilon_r$ of 6900 did not reach the objective value of less than 0.1%, the practical use in the high frequency range appeared to be difficult. On the other hand, although $\varepsilon_r$ in $0.9Pb(Mg_{1/3})$ $O_3\cdot0.1PbTiO_3$ (0.9PMN·0.1PT; PMNT 90/10) ceramic previously reported by Gupta et al.[4] attained to 35,000 at Curie temperature, this was not also the potential material for SIP applications on account of an abrupt change in temperature characteristic of $\varepsilon_r$ and a high

---

* Corresponding author.
*E-mail address:* kobune@chem.eng.himeji-tech.ac.jp (M. Kobune).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00575-2

tan$\delta$ of 4.6% in the vicinity of R.T. Accordingly, there are few inorganic dielectric materials well suited for the requirements of SIP applications.

The purpose of this study is to develop inorganic dielectric materials for the layer insulating materials with high dielectric constant and low dielectric loss of the next-generation SIP. In the present study, we attempt to restrain the formation of pyrochlore phase by adding a small amount of MgO to 0.94PMN·0.06PT (PMNT 94/6) and find out the excess MgO content to obtain the single-phase perovskite structure. Based on the obtained findings, after fabricating PMNT–PMWFT ceramics using $x\mathrm{Pb(Mg_{1/2}W_{1/2})O_3}\cdot(1-x)\mathrm{Pb(Fe_{1/2}Ta_{1/2})O_3}$ ($x$PMW·($1-x$)PFT; PMWFT $100x/100(1-x)$), which acts as a depressor to PMNT 94/6 with addition of excess MgO, the dielectric properties of the obtained specimens are investigated in detail. The effects of depressor addition on electrical properties of PMNT–PMWFT ceramics are consequently revealed.

## 2. Experimental

### 2.1. Specimen preparation

#### 2.1.1. $0.94\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}\cdot0.06\mathrm{PbTiO_3}$ (PMNT 94/6) specimens with addition of excess MgO

Regent-grade, PbO, $MgCO_3$, $Nb_2O_5$ and $TiO_2$ were used as starting materials. PMNT 94/6 powders were synthesized by the two-step solid-state reaction using a columbite precursor.[5] Two mass% polyvinyl alcohol (PVA) solution and 0–9 mass% MgO were added to the calcined PMNT 94/6 powders which were then ground for 12 h in a planetary zirconia wet ball mill. After drying the wet powders at 105 °C for 1.5 h, they were sieved using a 120 mesh (opening; 125 μm) screen. The granules were pressed at around 245 MPa into discs of 12 mm diameter and approximately 1.2 mm thickness. The resulting green compacts were placed in a high-purity MgO crucible and sintered at 1150 °C for 5 h in air by the powder-bed method using calcined powders with the same composition as the compacts.

#### 2.1.2. PMNT 94/6-$\mathrm{Pb(Mg_{1/2}W_{1/2})O_3}$–$\mathrm{Pb(Fe_{1/2}Ta_{1/2})O_3}$ specimens

The relaxor-ferroelectrics, $\mathrm{Pb(Mg_{1/2}W_{1/2})O_3}$ (PMW) and $\mathrm{Pb(Fe_{1/2}Ta_{1/2})O_3}$ (PFT) powders were also synthesized by the columbite route using $MgWO_4$ and $FeTaO_4$ precursors, respectively. After the PMNT, PMW and PFT powders inproportions appropriate to obtain the compositions $\mathrm{Pb(Mg_{1/3}Nb_{2/3})_{0.94x}Ti_{0.06x}O_3}$–$\mathrm{Pb(Mg_{1/2}W_{1/2})_{(1-x)y}(Fe_{1/2}Ta_{1/2})_{(1-x)(1-y)}O_3}$, where $x = 0.6$–$0.9$ and $y = 0.6$–$1.0$ were uniformly mixed, 2 mass% PVA solution and 1.0 mass% MgO were added to the mixtures which were then ground in the same wet ball mill described above. The following process was performed under the same conditions as the preparation process of PMNT specimens.

### 2.2. Measurement of physical properties

The crystalline phase was identified using an X-ray diffractometer (XRD; Rigaku, RINT1500). The microstructures of the fractured specimens were observed under a field-emission-type scanning electron microscope (FE-SEM; Hitachi, S-900). The average grain sizes were determined by the linear intercept method using FE-SEM photographs. The temperature dependence of the relative permittivity, $\varepsilon_r$, and the dielectric loss, tan$\delta$, was investigated at 1 kHz in the temperature range from −30 to 120 °C using a multi-frequency LCR meter (Yokogawa Hewlett-Packard, 4274A. The frequency dependence of $\varepsilon_r$ and tan$\delta$ was investigated at R.T. in the frequency range from 100 Hz to 1 MHz using an impedance analyzer (Hewlett-Packard, HP4194A) and a testing fixture (Agilent Tech., 16451B).

## 3. Results and discussion

### 3.1. $0.94\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}\cdot0.06\mathrm{PbTiO_3}$ (PMNT 94/6) specimens with addition of excess MgO

The XRD patterns of the PMNT 94/6 ceramics with the addition of 0–9 mass% excess MgO are shown in Fig. 1. As shown, it was confirmed that the specimen without the excess MgO addition had a slight amount of pyrochlore phase which was stable at low temperature besides the perovskite phase. Although the specimen with 1 mass% excess MgO hardly has the formation of the pyrochlore phase and non-reacted MgO, the excess MgO of more than 4 mass% yields the formation of a secondary phase, as observed in the vicinity of $2\theta = 42.9°$ in the figure. Based on the fact that MgO has

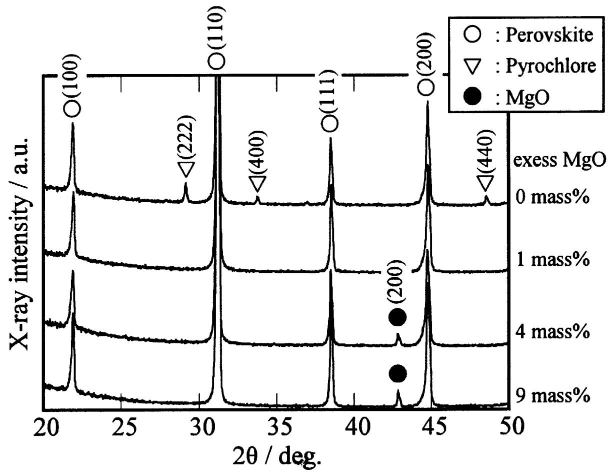

Fig. 1. XRD patterns of PMNT ceramics with the addition of 0–9 mass% excess MgO.

an extremely low $\varepsilon_r$ of 10–13.5,[6] MgO deposited in the PMNT microstructure is also considered to play a role of lowering $\varepsilon_r$, as well as in the case of the pyrochlore phase described above. It was thus ascertained from the above results that the addition of 1.0 mass% excess MgO was effective in restraining the formation of the pyrochlore phase and stabilizing the perovskite phase. The temperature dependence of $\varepsilon_r$ and tan$\delta$ for PMNT ceramics with the addition of 1.0 mass% excess MgO was moreover investigated. The temperature–$\varepsilon_r$ curve, which had $\varepsilon_r$ of 17,750 at 25 °C and the maximum value of 20,210 at approximately 40.2 °C. On the other hand, tan$\delta$ abruptly changed from 7.55% (at 5.9 °C) to 0.09% (at 60 °C) in the temperature range of 5.9–60 °C. Accordingly, the temperature characteristics of $\varepsilon_r$ and tan$\delta$ of the PMNT ceramics with the addition of 1.0 mass% excess MgO were not yet sufficiently satisfied with the purpose of this study.

### *3.2. PMNT–PMWFT specimens with compositions xPMNT 94/6-(1−x)PMWFT 85/15, where x = 0.6–0.9*

To restrain the formation of the pyrochlore phase and promote the densification of the microstructure, the depressor with a composition of $0.85\mathrm{Pb}(\mathrm{Mg}_{1/2}\mathrm{W}_{1/2})\mathrm{O}_3 \cdot 0.15\mathrm{Pb}(\mathrm{Fe}_{1/2}\mathrm{Ta}_{1/2})\mathrm{O}_3$ (PMWFT 85/15) was added in the range of 10–40 mol% to PMNT 94/6 with the addition of 1.0 mass% excess MgO.

It was ascertained from the XRD results of the obtained PMNT–PMWFT ceramics and PMWFT 85/15 ceramic as a reference that the substitutional limit of PMWFT 85/15 to PMNT was approximately 20 mol% under the present processing conditions. The frequency dependence of $\varepsilon_r$ and tan$\delta$ for PMNT–PMWFT ceramics with compositions $x$PMNT 94/6-(1−$x$)PMWFT 85/15, where $x = 0.6$–$0.9$ is shown in Fig. 2. As shown, $\varepsilon_r$ of the four specimens exhibited almost constant values in the range of 100 Hz–1 MHz independent of a change in the frequency. Especially, the $\varepsilon_r$ values of $x = 0.9$ and 0.8 specimens were 9410 and 4660, respectively and were sufficiently satisfied with the objective value ($\varepsilon_r \geqslant 1000$ at 1 MHz) of this study, while only the $x = 0.9$ specimen exhibited relatively high tan$\delta$ (0.4%) of more than 0.1% at 1 MHz. This means that with the depressor addition of 10 mol% to PMNT, no densification of the microstructure may be sufficiently carried out. The 0.8PMNT 94/6·0.2PMWFT 85/15 specimen was consequently determined to be a promising inorganic dielectric material among the four studied here.

### *3.3. PMNT–PMWFT specimens with compositions 0.8PMNT 94/6–0.2PMWFT 100y/100(1−y), where y = 0.6–1.0*

Based on the findings that good dielectric properties were obtained when the mixing proportion (mol%) of PMNT 94/6/PMWFT 85/15 was 80/20, the improvement in dielectric properties was further examined by fixing the ratio of PMNT/PMWFT = 80/20 and varying the mixing proportion of the two relaxor-ferroelectrics (PMW and PFT) in PMWFT.

Fig. 3 shows the FE-SEM photographs of fractured surfaces for (a) $y = 1.0$ and (b) 0.7 of PMNT–PMWFT ceramics. As shown, the grain size significantly increased with increasing PFT content in PMWFT. The average grain sizes of the $y = 1.0$ and 0.7 specimens were estimated to be approximately 8.5 and 10.9 μm, respectively. This result may be explained by the presumption that the grain growth occurred due to the firing at the fixed high temperature (= 1150 °C) in spite of a reduction in the real sintering temperature of PMNT–PMWFT solid solution with increasing PFT content. The temperature dependence of $\varepsilon_r$ and tan$\delta$ for PMNT–PMWFT ceramics with compositions 0.8PMNT 94/6–0.2PMWFT 100$y$/100(1−$y$), where $y = 0.6$–$1.0$ is shown in Fig. 4. As shown, $\varepsilon_r$ at 25 °C decreases from

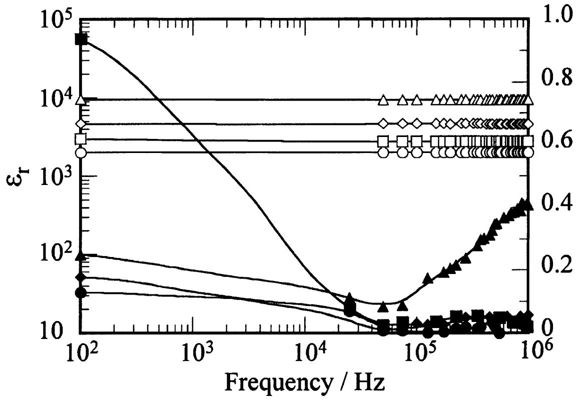

Fig. 2. Frequency dependence of $\varepsilon_r$ and tan$\delta$ for PMNT–PMWFT ceramics with compositions $x$PMNT 94/6–(1−$x$)PMWFT 85/15, where $x = 0.6$–$0.9$. $\varepsilon_r$: $x = 0.6$ (○), 0.7 (□), 0.8 (◇) and 0.9 (△), tan$\delta$: $x = 0.6$ (●), 0.7 (■), 0.8 (◆) and 0.9 (▲).

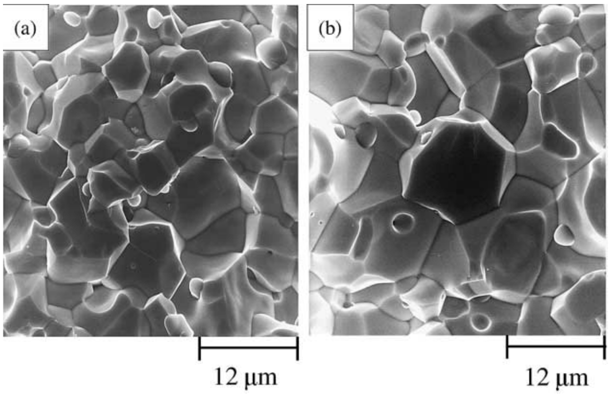

Fig. 3. FE-SEM photographs of fractured surfaces for (a) $y = 1.0$ and (b) $y = 0.7$ of PMNT–PMWFT ceramics with compositions 0.8PMNT 94/6–0.2PMWFT 100/100(1−$y$).

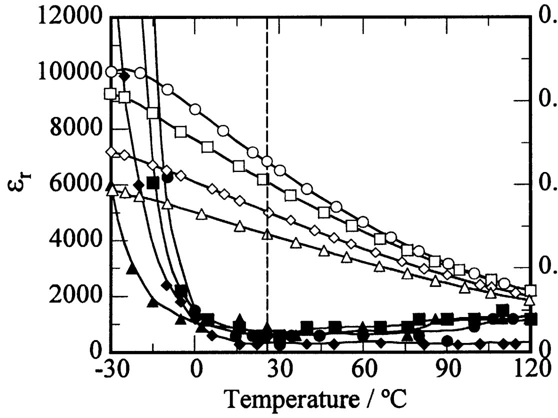

Fig. 4. Temperature dependence of $\varepsilon_r$ and tan$\delta$ for PMNT–PMWFT ceramics with compositions 0.8PMNT 94/6–0.2PMWFT 100$y$/100(1−$y$). $\varepsilon_r$: $y=0.6$ (○), 0.7 (□), 0.85 (◇) and 1.0 (△), tan$\delta$: $y=0.6$ (●), 0.7 (■), 0.85 (◆) and 1.0 (▲).

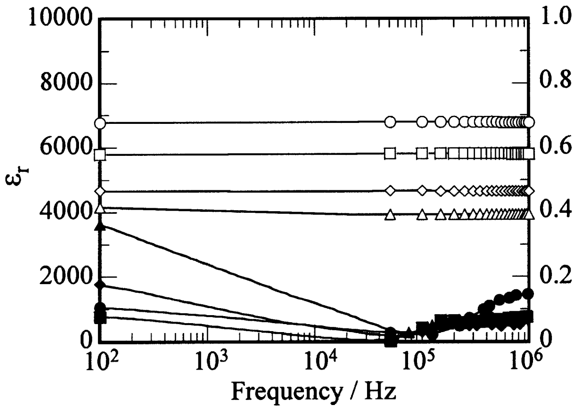

Fig. 5. Frequency dependence of $\varepsilon_r$ and tan$\delta$ for PMNT–PMWFT ceramics with compositions 0.8PMNT 94/6–0.2PMWFT 100$y$/100(1−$y$). $\varepsilon_r$: $y=0.6$ (○), 0.7 (□), 0.85 (◇) and 1.0 (△), tan$\delta$: $y=0.6$ (●), 0.7 (■), 0.85 (◆) and 1.0 (▲).

6810 ($y=0.6$) to 4240 ($y=1.0$) with increasing PMW content. Consequently, for the relationship between the grain size and $\varepsilon_r$, $\varepsilon_r$ showed a tendency to become higher as the grain size increased. On the other hand, the temperature-tan$\delta$ curves showed a tendency to shift toward low temperature side with increasing PMW content, whereas tan$\delta$ at 25 °C maintained extremely low values of 0.02–0.03% regardless of the PMW content. Fig. 5 shows the frequency dependence of $\varepsilon_r$ and tan$\delta$ for PMNT–PMWFT ceramics with compositions 0.8PMNT 94/6–0.2PMWFT 100$y$/100(1−$y$), where $y=0.6$–1.0. As shown, $\varepsilon_r$ of the four specimens is hardly dependent on the frequency in the range of 100 Hz–1 MHz. However, it is apparent from the figure that the amplitude of $\varepsilon_r$ is strongly affected by the mixing proportion of PMW/PFT in PMWFT. On the other hand, although tan$\delta$ of the $y=0.6$ specimen increased to 0.15% at 1 MHz, that of the $y=0.7$–1.0 specimens was rather low (0.06–0.08%). It is hence concluded that the 0.8PMNT 94/6·0.2PMWFT 70/30 ceramics having high $\varepsilon_r$ of 5810, low tan$\delta$ of 0.07% at 1 MHz and their flat frequency characteristics in the vicinity of R.T., which show great promise as inorganic dielectric materials for the layer insulating materials with high $\varepsilon_r$ and low tan$\delta$ of the next-generation SIP.

## 4. Conclusions

With the addition of 1.0 mass% excess MgO to $0.94Pb(Mg_{1/3}Nb_{2/3})O_3{\cdot}0.06PbTiO_3$ (PMNT 94/6), the formation of the pyrochlore phase was effectively restrained, resulting in an acquisition of high $\varepsilon_r$ of 17750 at 25 °C. When the mixing proportion (mol%) of PMNT 94/6/PMWFT 85/15 was 80/20, good dielectric properties with relative permittivity, $\varepsilon_r$ of 4660 and dielectric loss, tan$\delta$ of 0.06% at 1 MHz were obtained. By varying the mixing proportion of PMW/PFT in PMWFT, which plays an important role of depressor to PMNT, 0.8PMNT 94/6·0.2PMWFT 70/30 ceramics having high $\varepsilon_r$ of 5810, low tan$\delta$ of 0.07% at 1 MHz and their flat frequency characteristics were obtained by means of the effects of depressor addition to PMNT and were well suited for the requirements of system-in-a-package applications.

## Acknowledgements

This work was partly supported by the Fundamental Technology Research Promotion Project in '01 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

## References

1. Fujimura, K., Hitotsuya, M., Yamano, S. and Higashida, H., 76 GHz millimeter-wave radar for ACC. *Proc. Int. Symp. Automot. Technol. Autom.*, 1999, **32**, 175–182.
2. Smolenskii, G. A., Agranovskaya, A. I. and Popov, S. N., Letters to the editor on the mechanism of polarization in solid solutions of $Pb_3NiNb_2O_9$–$Pb_3MgNb_2O_9$. *Soviet Physics-Technical Physics*, 1958, 1380.
3. Ogasawara, T. and Mito, Y., PMN-based ceramic capacitors. *Electronic Ceramics*, 1991, **22**, 51–55.
4. Gupta, S. M., Bedekar, P. R. and Kulkarni, A. R., Synthesis, dielectric and microstructure studies of lead magnesium niobate stabilised using lead titanate. *Ferroelectrics*, 1996, **189**, 17–25.
5. Swartz, S. L. and Shrout, T. R., Fabrication of perovskite lead magnesium niobate. *Mat. Res. Bull.*, 1982, **17**, 1245–1250.
6. Kobune, M., Single crystal substrates. In *Handbook of Ceramics*, 2nd edn. The Ceramic Society of Japan, Gihodoshuppan, Tokyo, 2002, pp. 922–924.