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Dielectric characters of $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$ ceramics fabricated at ultra-low temperature by the spark-plasma-sintering method

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Abstract

Solid solution $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ shows high dielectric constant near room temperature and is an ideal capacitor material. The composition $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$, which is located near the morphotropic phase boundary, were densified by the spark-plasma-sintering method at an ultra-low temperature (700 °C). Dielectric constant measurement shows that the thus prepared sample shows higher dielectric constant at room temperature and good temperature stability in a wide temperature range. The behavior is much different from that of samples sintered by conventional method and could be ascribed to size effect.

Keywords: Spark-plasma-sintering; Ceramics; MLCC; Lead magnesium niobate–lead titanate

1. Introduction

The multi-layer ceramic capacitors (MLCC), which can store electric energy in the form of an electrostatic field, are used in electric devices such as mobile telephones, computers, electronic lighting and high-voltage circuits among others. Accompany the miniaturization in size of electric devices, the challenges to MLCC industries include achieving a useful capacitance value at a reasonable price in a small size.

Conventionally, expensive noble metal such as Pt or Pd is used as internal electrode of MLCC due to their stability at high temperature. However, with an increased number of stacked layers due to miniaturization and higher capacitance of MLCCs, the percentage of the electrode cost in the overall cost increases sharply. It is strongly desired that the expensive internal electrode Pt or Pd could be replaced by base metals Ni or Cu to decrease the overall cost. However, the melting point (T_{mp}) is lower than that for base metals (e.g. T_{mp} (Cu) = 1080 °C). Thus, a low-temperature ($<T_{mp}$) sintering is required. Many studies aimed at lowering the sintering temperature have been reported. They include the addition of sintering aids with low melting point [1,2], reactive sintering method which unifying calcination and sintering, fast firing method which is directly introducing the sample into a furnace maintained around 900 °C, the usage of calcined material with reduced particle size by planetary ball milling and the spark plasma sintering method [3–5], and so on.

The spark-plasma-sintering (SPS) method, which is used to be used to densify metals, has recently been used to densify dielectric materials. SPS is characterized by the charging between powder particles with electrical energy and uniaxial sintering pressure. Sintering is carried out in vacuum to protect dies from oxidization. Therefore, in many cases of oxide materials sintering, post annealing is needed to recover from partial reduction.

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), is a well-known relaxor ferroelectric. It exhibits a diffused phase transition and anomalously large frequency dependent dielectric maxima. Its solid solution with $PbTiO_3$ (PT), $(1 - x)$PMN–xPT, shows exceptional high dielectric constant near room temperature at $x \sim 0.3$, and is an ideal dielectric for capacitors. In the present research, 0.7PMN–0.3PT powders were densified

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by the SPS technique at an ultra-low temperature (700 °C) and its dielectric properties have been investigated.

2. Experimental

The 0.7PMN–0.3PT powder (Cerone Inc.) was charged into a die made of tungsten carbide and heated to 700 °C under a uniaxial pressure of 500 MPa in vacuum. Heating rate was 400 °C/min. After holding at the temperature (700 °C) for 5 min, heating was stopped and the pressure was released. Due to the usage of tungsten carbide die and being sintered under vacuum atmosphere, the as-sintered pellet was slightly reduced, and an additional oxidization process was necessary. Therefore, the as-sintered sample was annealed at 700 °C for 12 h. To avoid the decomposition of the perovskite phase to the pyrochlore phase during the oxidization process, the as-sintered pellet has been annealed under the PbO-rich atmosphere by placing $PbZrO_3$ under the sample. During the annealing process, the sample was separated from the $PbZrO_3$ by a Pt foil. After the annealing process, the density was first measured using the Archimedes method, the microstructure was observed using the scanning electron microscopy (SEM, Hitachi FE-SEM S-5000), and the composition was confirmed by X-ray diffraction pattern (XRD, Philips Co. Ltd., X'pert PRO). For dielectric constant measurement, the pellet was polished and the silver paste was applied onto the both surfaces as electrodes. The dielectric constant was determined with an impedance analyzer (Agilent 4294A) over the temperature range of 25–300 °C.

3. Results and discussion

Density measurement result shows that the sample has been successfully densified by the SPS method. The relative density is over 98%. The temperature dependence of the dielectric constant (ε) and the dielectric loss in the cooling run is shown in Fig. 1. ε is about 3700 at room temperature. With increasing temperature from room temperature, ε slowly increases at first, shows a broad maximum at around 50 °C, and then decreases monotonically. The maximum dielectric constant (ε_{max}) is about 3900. The dielectric loss (tan δ) is about 3.3% at room temperature and decreases with increasing temperature till about 220 °C and then turned to increase slowly. The minimum tan δ value (~0.75%) is found around 220 °C. The behavior is different from previous reports [6,7]. Previous reports show that, ε for 0.7PMN–0.3PT sintered using conventional method maximizes at around 150 °C and ε_{max} could be as high as 35,000.

To confirm the composition of the pellet, the pellet was annealed at 1200 °C for 12 h under the Pb-rich atmosphere and the temperature dependence of the dielectric constant and the dielectric loss were measured again. The results are shown in Fig. 2. ε is about 2200 at room temperature. It increases strongly with increasing temperature and peaked at around 145 °C. ε_{max} equals to 33,200. The room temperature value of tan δ is 3.3%, same as that after annealed at 700 °C. The sudden change around 150 °C corresponds to the peak temperature for ε. The

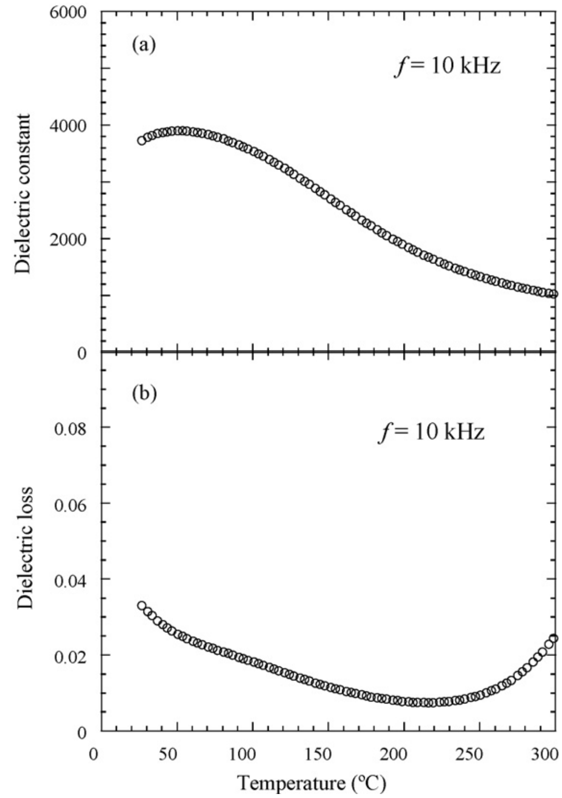

Fig. 1. Temperature dependence of (a) dielectric constant and (b) dielectric loss at 10 kHz after annealed at 700 °C for 12 h.

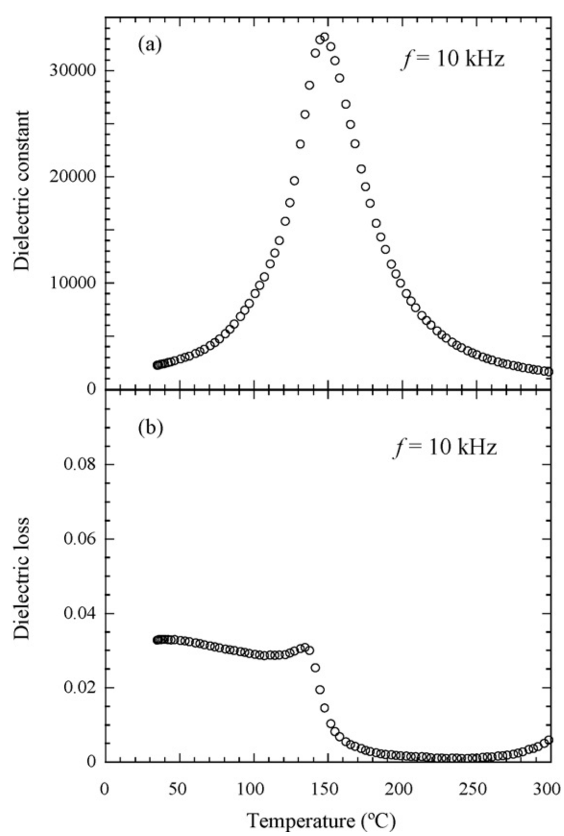

Fig. 2. Temperature dependence of (a) dielectric constant and (b) dielectric loss at 10 kHz after annealed at 1200 °C for 12 h.

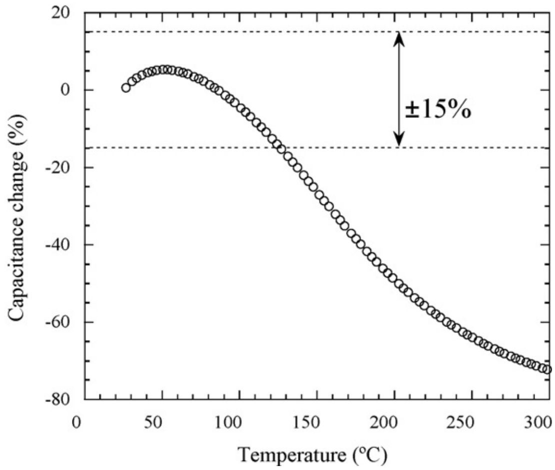

Fig. 3. Change in dielectric constant (capacitance) at 10 kHz in the temperature range between room temperature and 300 °C.

above values are well consistent with previous reports [6,7] and indicate that the composition of the pellet is a stoichiometric 0.7PMN–0.3PT.

Fig. 3 shows the change in dielectric constant (capacitance), $(\varepsilon_T - \varepsilon_{RT})/\varepsilon_{RT}$, at 10 kHz between room temperature and 300 °C after annealed at 700 °C. The temperature stability is fairly good over a wide temperature range. The change is less than +5% and −15% in the temperature range of 25–125 °C. The data shown in Fig. 3 is compatible to the Z7R capacitor specification ($\Delta\varepsilon < \pm 15\%$ at 10–125 °C). Currently, the capacitor materials for Z7R specification are modified $BaTiO_3$. These materials show 4000–5000 of dielectric constant values at room temperature and is usually sintered at temperatures higher than 1100 °C.

The annealing process affects the physical properties of the pellet in two aspects. One is to get sample to be oxidized and another is to make the growth of the particle size. Fig. 4 shows the SEM images for the pellet observed after annealed at 700 and 1200 °C, respectively. The mean grain size, which was determined by the linear intercept method from the SEM images, is about 0.4 μm after annealed at 700 °C and 6.4 μm after annealed at 1200 °C. Compared to that after annealed at 700 °C, the grain size after annealed at 1200 °C is over 15 times bigger.

It is well known that grain size can have a dramatic influence on crystal structure and properties for ferroelectric ceramics. Researches on $BaTiO_3$ have shown that high dielectric constant could be observed in fine-grained samples. Anan'eva et al. [8] reported a dielectric constant of 6000 for a chemically pure $BaTiO_3$; while the dielectric constant is only 1200–1500 when grain size is large (>1 μm). When grain size is finer than a critical size (10–20 nm), $BaTiO_3$ could lose its ferroelectricity [9–12]. In Fig. 5, the XRDs of before sintering and after annealed at 1200 °C are compared. The structure remains single perovskite and no peak shift has been observed. The results indicate that the composition is the same before and after the annealing process. Therefore, we believe that the behavior shown in Fig. 1 sample can be ascribed to the size effect.

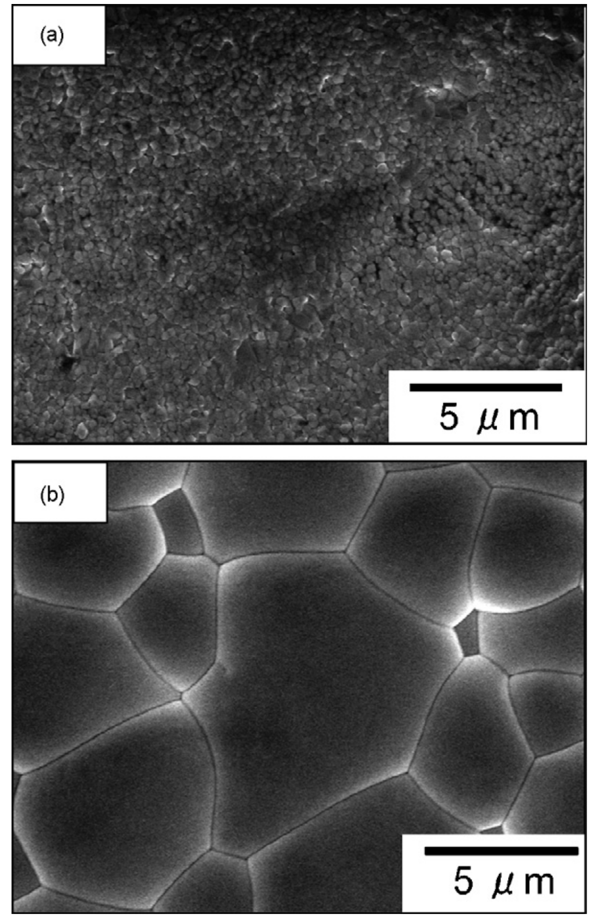

Fig. 4. SEM images taken after annealed at (a) 700 °C and (b) 1200 °C for 12 h.

In Table 1, the physical properties after annealed at 700 and 1200 °C are summarized. Compared to conventional sintered sample, our $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$ sample is characterized by higher dielectric constant value at room temperature and nice temperature stability over a wide temperature range. These are characters demanded by good MLCC materials. Furthermore, the fabricating temperature (SPS sintering at 700 °C + annealing at 700 °C) is much lower than the melt point

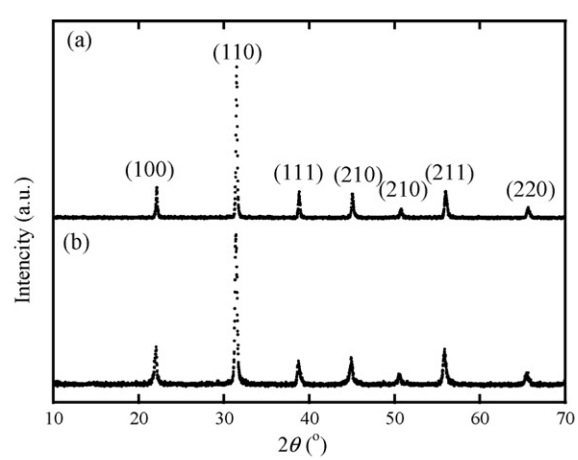

Fig. 5. XRD taken (a) before sintering and (b) after annealed at 1200 °C for 12 h.

Table 1
Summarization of physical properties

Annealing temperature (°C)	Mean grain size (μm)	T_m (°C)	ε_{RT}	ε_{max}	tan δ_{RT} (%)
700	0.4	52	3700	3900	3.3
1200	6.4	145	2200	33,000	3.3

of base metals and makes the cofiring with either Ni or Cu be possible. Therefore, the SPS process is promising for fabricating MLCC materials at low temperature.

4. Conclusions

Solid solution $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ with $x = 0.3$, has been densified by the spark-plasma-sintering method at an ultra-low temperature (700 °C). Dielectric constant measurement shows that thus prepared sample has higher dielectric constant at room temperature and good temperature stability in a wide temperature range, which is comparable to that of Z7R capacitor specification ($\Delta\varepsilon < \pm 15\%$ at 10–125 °C). The temperature dependence of dielectric constant is much different from that of samples sintered by using conventional method. SEM observation shows that the mean grain size is about 0.4 μm. It is considered that the reason for the behavior is the size effect which has been extensively studied on $BaTiO_3$.

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