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Piezoelectric properties of $Pb(Mn_{1/3}Nb_{2/3})O_3–PbZrO_3–PbTiO_3$ ceramics with sintering aid of $2CaO–Fe_2O_3$ compound

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Abstract

Since the electromechanical devices move towards enhanced power density, high mechanical quality factor (Q_m) and electromechanical coupling factor (k_p) are commonly needed for the high powered piezoelectric transformer with $Q_m \geq 2000$ and $k_p = 0.60$. Although $Pb(Mn_{1/3}Nb_{2/3})O_3–PbZrO_3–PbTiO_3$ (PMnN–PZ–PT) ceramic system has potential for piezoelectric transformer application, further improvements of Q_m and k_p are needed. Addition of $2CaO–Fe_2O_3$ has been proved to have many beneficial effects on $Pb(Zr,Ti)O_3$ ceramics. Therefore, $2CaO–Fe_2O_3$ is used as additive in order to improve the piezoelectric properties in this study. The piezoelectric properties, density and microstructures of $0.07Pb(Mn_{1/3}Nb_{2/3})O_3–0.468PbZrO_3–0.462PbTiO_3$ (PMnN–PZ–PT) piezoelectric ceramics with $2CaO–Fe_2O_3$ additive sintered at 1100 and 1250 °C have been studied. When sintering temperature is 1250 °C, Q_m has the maximum 2150 with 0.3 wt.% $2CaO–Fe_2O_3$ addition. The k_p more than 0.6 is observed for samples sintered at 1100 °C. The addition of $2CaO–Fe_2O_3$ can significantly enhance the densification of PMnN–PZ–PT ceramics when the sintering temperature is 1250 °C. The grain growth occurred with the amount of $2CaO–Fe_2O_3$ at both sintering temperatures.

Keywords: A. Calcination; C. Piezoelectric properties; Sintering aids; $Pb(Zr,Ti)O_3$

1. Introduction

The piezoelectric ceramic materials of $Pb(Zr, Ti)O_3$ (PZT) have many technical applications such as actuators and transformers because of its excellent piezoelectric properties. PZT is normally sintered between 1200 and 1300 °C. The vaporization of PbO in its composition during sintering is great significance, which makes it difficult to control the microstructure and electromechanical properties and also causes the environmental pollution. Recently, multilayer piezoelectric ceramic devices have been widely investigated and applied [1–4]. This is because these multilayer piezoelectric devices provide advantages of low power consumption and low driving voltage than conventional piezoelectric ceramic devices. For multilayer components and thick-film devices, it is desirable to reduce the sintering temperature. This will make it possible to co-fire internal electrodes with lower melting point in the ceramics, such as silver–palladium alloys [5]. The low temperature sintering of PZT ceramics can not only solve the problems from the vaporization of PbO, further, reduce the energy consumption and the fabrication cost.

A lot of efforts have been done during the last two decades to reduce the sintering temperature of PZT while retaining good piezoelectric properties. Among the methods investigated are sintering the ultra-fine powders [6] and sintering aids with low melting points [7–9]. Additives that result in a liquid-phase formation at temperatures well below the traditional sintering temperature make it possible to achieve a dense material by liquid phase sintering.

CaO and Fe_2O_3 were used as additive to improve the piezoelectric properties in the previous researches [10,11]. Furthermore, $CaO–Fe_2O_3$ compound had been used to modify PZT ceramics, to improve high field sustaining capability and electric dissipation [12]. In the case of piezoelectric transformer application, sometimes the piezoelectric ceramics with mechanical quality factor (Q_m) $\geq$ 2000 and electromechanical planar coupling factor (k_p) $\geq$ 0.6 are required. This is a quite great challenge to develop the materials with these piezoelectric properties. Also the sinter-

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ing temperature of those ceramics should be as low as possible. In this work, $0.07Pb(Mn_{1/3}Nb_{2/3})O_3$–$0.468PbZrO_3$–$0.462PbTiO_3$ [13,14] ceramics were sintered at 1100 and 1250 °C with compound of $2CaO$–Fe_2O_3. Effect of sintering aid content on piezoelectric properties, density and microstructure were studied.

2. Experimental procedures

Raw materials of 0.07PMnN–0.468PZ–0.462PT with 2 wt.% excess PbO were prepared with starting materials of PbO, TiO_2, ZrO_2, MnO and Nb_2O_5. $MnNb_2O_6$ was prepared by columbite process first, then wet-mixed with PbO, TiO_2 and ZrO_2. The designated composition mixed powders were calcined at 850 °C for 3 h. $2CaO$–Fe_2O_3 was made from mixture of $CaCO_3$ and Fe_2O_3 with molar ratio 2:1, and calcinated at 1100 °C for 2 h. Different contents of $2CaO$–Fe_2O_3 were added in 0.07PMN–0.468PZ–0.462PT and pressed into pellets with 17 mm diameter and 1.5 mm thickness at 1250 kg/cm^2. Pellets were sintered at 1100 and 1250 °C for 3 h in lead protected atmosphere. After sintering, the surfaces of the disks were polished and painted with silver paste fired at 590 °C for 12 min. The poling was done in silicon oil at 120 °C with applied static field of 4 kV/cm for 30 min.

The microstructures of fractured sample were analyzed by means of a scanning electron microscope (SEM, Type: JEOL-5600). The Q_m, k_p, and tangent loss ($\tan\delta$)were measured by HP 4194A impedance analyzer. The sintered density of the samples was measured using Archimedes' principle.

3. Results and discussion

The results of piezoelectric properties Q_m and k_p with different content of $2CaO$–Fe_2O_3 sintered at 1100 and 1250 °C are shown in Figs. 1 and 2. Small variations of Q_m can be observed with additive up to 0.2 wt.% at 1250 °C and the maximum happened at the content of 0.3 wt.%. When $2CaO$–Fe_2O_3 contents are higher than 0.3 wt.%, the Q_m dropped sharply. The values of Q_m when sintered at 1100 °C shows that small quantity of $2CaO$–Fe_2O_3 will increase the Q_m up to 2000. However, in the additive contents more than 0.05 wt.%, the Q_m will be decreased slightly until 0.3 wt.%. For $2CaO$–Fe_2O_3 content greater than 0.3 wt.%, the result is similar to those of sample sintered at 1250 °C, the Q_m also drops sharply. Fig. 2 shows the behaviors of k_p as a function of the dopant content for two sintering temperatures. The k_p presented the values between 0.585 and 0.625 with the increase of $2CaO$–Fe_2O_3 at 1100 °C. For the results of higher sintering temperature of 1250 °C, a significant drop happened with the amount of additive more than 0.2 wt.%.

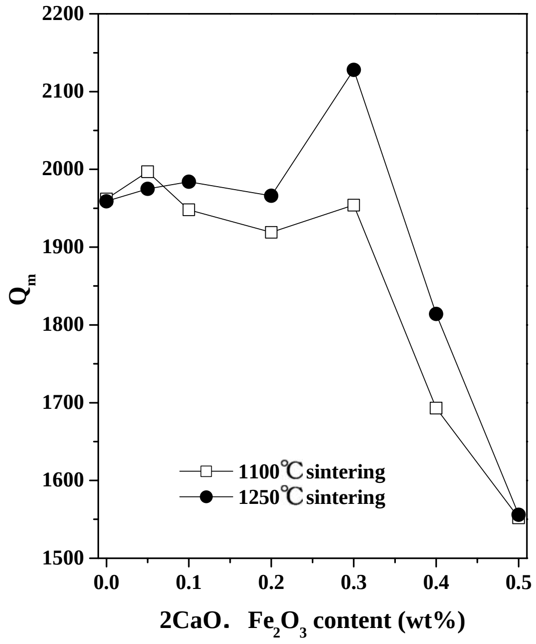

Fig. 1. Mechanical quality factor (Q_m) of 0.07PMnN–0.468PZ–0.462PT ceramics sintered at 1100 and 1250 °C with various $2CaO$–Fe_2O_3 additions.

The behavior of $\tan\delta$ as various $2CaO$–Fe_2O_3 contents of two sintering temperatures was shown in Fig. 3. The $\tan\delta$ has constant steadily as the increase of additive at both sintering temperatures when the content of $2CaO$–Fe_2O_3 is less than 0.3 wt.%. A sharp raise happened as the content of additive more than 0.3 wt.%. Domain wall motion is inherently a loss process, the inhibition of domain motion reduces the dielectric loss, and therefore Q_m is enhanced. Using a

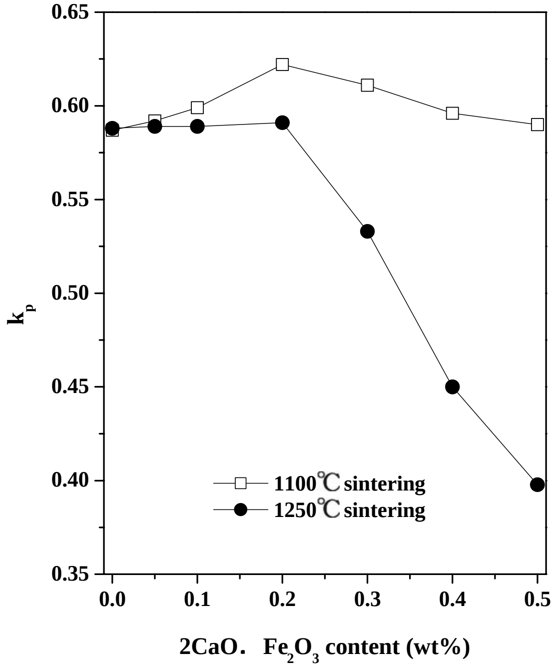

Fig. 2. Electromechanical planar coupling coefficient (k_p) vs. $2CaO$–Fe_2O_3 content for samples sintered at 1100 and 1250 °C.

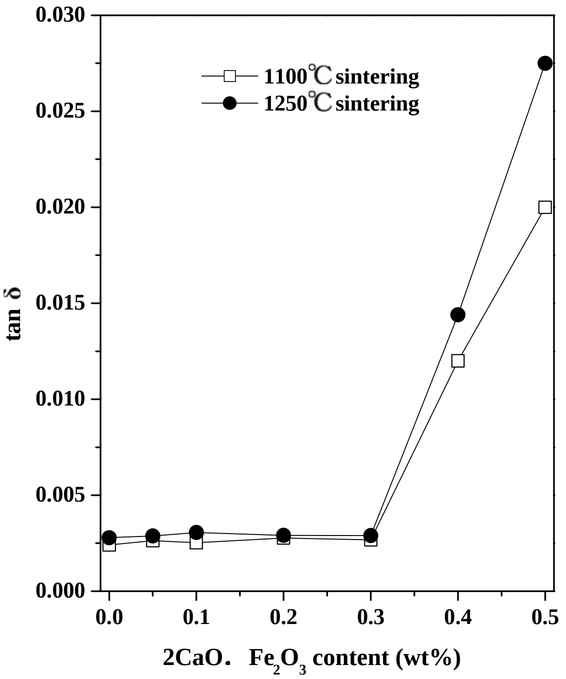

Fig. 3. Effect of 2CaO–Fe_2O_3 content on dielectric loss ($\tan \sigma$) in two sintered 0.07PMnN–0.468PZ–0.462PT ceramics.

thermodynamic method that utilizes the expression for the free energy of the piezoelectric ceramic system, linear relationship between ${Q_\mathrm{m}}^{-1}$ and $\tan \delta$ has been established [15]. Based on the assumption of 90° domain walls motion, similar result has been demonstrated by Gerthsen et al. [16].

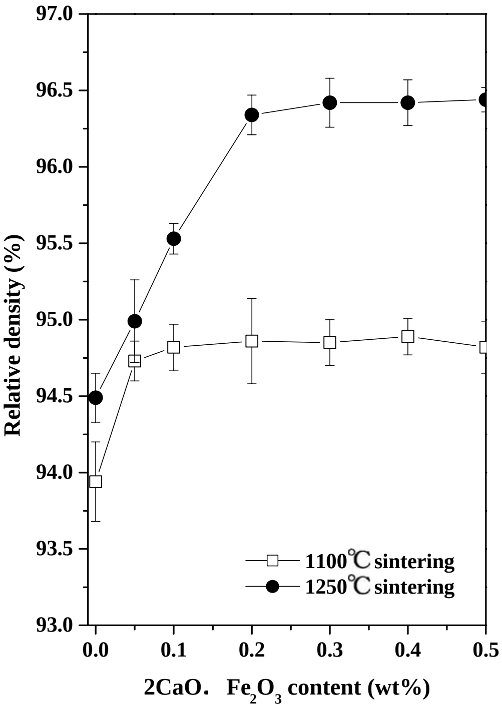

Fig. 4. Relative density of 0.07PMnN–0.468PZ–0.462PT ceramics with different content of 2CaO–Fe_2O_3 sintered at 1100 and 1250 °C.

Furthermore, an investigation of the effects of small addition of Fe_2O_3 to PZT ceramics [17] has also shown that the decrease of dielectric loss is accompanied with the increase of mechanical quality factor. Comparing Figs. 1 and 3

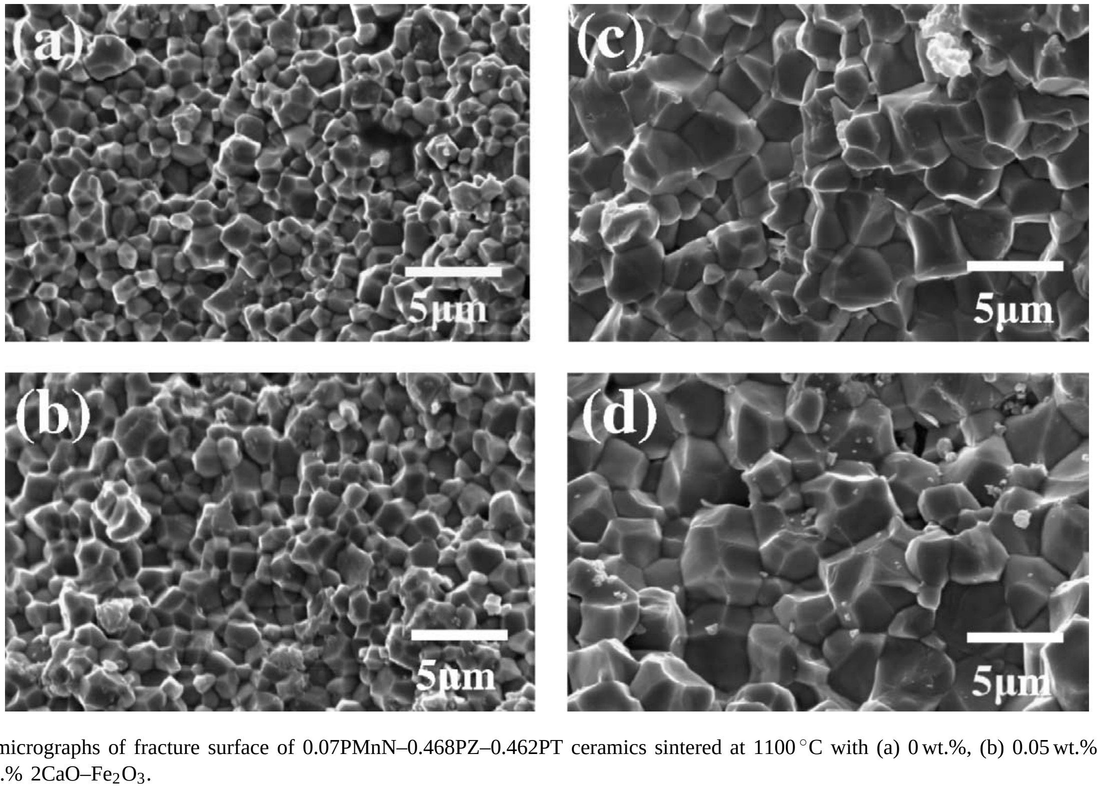

Fig. 5. SEM micrographs of fracture surface of 0.07PMnN–0.468PZ–0.462PT ceramics sintered at 1100 °C with (a) 0 wt.%, (b) 0.05 wt.%, (c) 0.3 wt.% and (d) 0.5 wt.% 2CaO–Fe_2O_3.

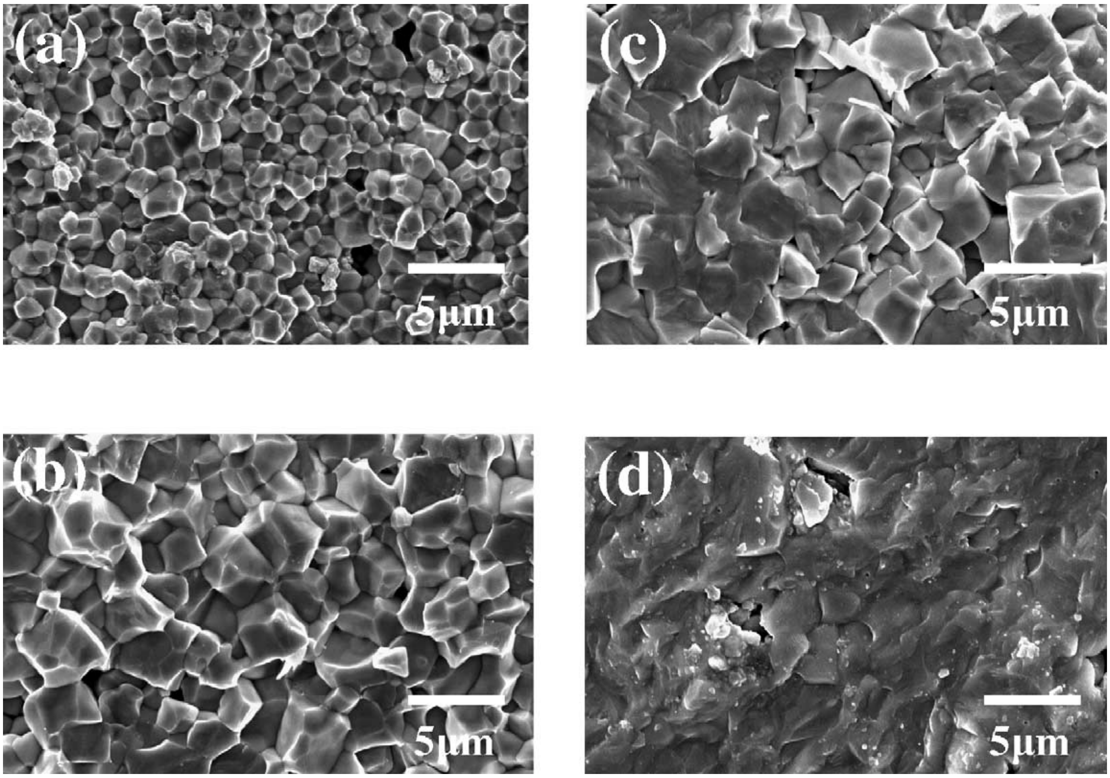

Fig. 6. SEM micrographs of fracture surface of 0.07PMnN–0.468PZ–0.462PT ceramics sintered at 1250 °C with (a) 0 wt.%, (b) 0.05 wt.%, (c) 0.3 wt.% and (d) 0.5 wt.% $2CaO–Fe_2O_3$.

in this study, the relationship between tan δ and Q_m is obviously correlated, especially for addition of $2CaO–Fe_2O_3$ more than 0.3 wt.%.

Fig. 4 shows the results of relative density of PMnN–PZ–PT sintered bodies with different contents of $2CaO–Fe_2O_3$. From the results, it is obvious that $2CaO–Fe_2O_3$ can only enhance the densification of PMnN–PZ–PT ceramics sintered at 1250 °C. Since the liquid phase sintering should take place when sintering was done at 1250 °C, the amount of $2CaO–Fe_2O_3$ will relate to the quantity of the liquid phase in the sintered body, and as a result, affect the densification of sintered ceramics. For case of sintering at 1100 °C, it is not surprised that there is no much effect of $2CaO–Fe_2O_3$ addition on the densification.

Fracture surfaces of the samples sintered at 1100 and 1250 °C with the selected contents of $2CaO–Fe_2O_3$ are shown in Figs. 5 and 6. It is clearly that PMnN–PZ–PT ceramics has similar gain size at both sintering temperatures without $2CaO–Fe_2O_3$. The relative density data shows that 1250 °C sintered samples has higher relative density, and the microstructure result reveals that high sintering temperature does not increase the grain size of PMnN–PZ–PT ceramics without additives. When small amount such as 0.05 wt.% of $2CaO–Fe_2O_3$ was added in PMnN–PZ–PT ceramics, the grain size is different for two sintering conditions. The grain growth is obvious for 1250 °C sintered sample. Increasing $2CaO–Fe_2O_3$ content up to 0.3 wt.%, grain growth was also observed in the samples sintered at 1100 °C. Apparently, $2CaO–Fe_2O_3$ addition has some effects on promotion of grain growth. For samples containing more than 0.3 wt.% of $2CaO–Fe_2O_3$, the fracture mode depends on the sintering temperature. Only intergranular fracture surface was observed in 1100 °C sintered samples. A mixture of intergranular and intrangranular fracture (Fig. 6c) and fully transgranular fracture (Fig. 6d) are clearly indicated. This means that $2CaO–Fe_2O_3$ can improve the mechanical strength of grain boundary when the sintering temperature is 1250 °C.

4. Conclusions

0.07PMnN–0.468PZ–0.462PT piezoelectric ceramics has been sintered at 1100 and 1250 °C using the compound $2CaO–Fe_2O_3$ additive. When sintering temperature is 1250 °C, the Q_m has the maximum 2150 with 0.3 wt.% $2CaO–Fe_2O_3$ addition. PMnN–PZ–PT ceramics containing $2CaO–Fe_2O_3$ more than 0.3 wt.% show a sharp drop of the Q_m, whether the sintering temperature is 1100 or 1250 °C. These results are closely related to those of tan δ. The k_p is slightly improved to 0.6 for samples sintered at 1100 °C with the various contents of $2CaO–Fe_2O_3$. On the other hand, samples sintered at 1250 °C show that their k_p's are independent of additive content while the content is less than 0.2 wt.%. Furthermore, the k_p drop dramatically occurred in $2CaO–Fe_2O_3$ addition larger than 0.2 wt.%.

When sintering temperature is at 1250 °C, $2CaO–Fe_2O_3$ as an additive can enhance the densification of PMnN–PZ–PT ceramics. Even the densification is not significant for the samples containing larger amount of $2CaO–Fe_2O_3$ and sintered at 1100 °C, the grain growth was observed.

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