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The microstructure and characteristics of 0.875PZT–0.125PMN ceramics with addition of Pb-based flux

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Abstract

The paper tries to prepare dense piezoceramics by way of reactive liquid phase sintering. Technique concerning a low-temperature sinterable process is developed by incorporating $4PbO.B_2O_3$. The host system is a perovskite type piezoceramics, $0.875Pb(Ti,Zr)O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$. It is clear that PbO deficiency of PMN-based relaxor can result in an excessive amount of pyrochlore phase which causes poor densification and greatly degraded dielectric properties. Additives, such as the Pb-based flux, $4PbO{\cdot}B_2O_3$, that increase the amount of PbO also reduce the fraction of pyrochlore phase of PMN-based. If small amounts of $4PbO{\cdot}B_2O_3$ glass powder are added to the calcined 0.875PZT–0.125PMN ceramics, the liquid pase is formed during sintering. Hence, the piezoelectric and dielectric properties are enhanced and the sintering temperature can be reduced. Grain growth in ceramics with sintering time and amounts of $4PbO{\cdot}B_2O_3$ dopants was also studied. The grain growth was analyzed from the kinetic grain growth equation: $R^n = k \times t$. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Grain growth; Piezoelectric properties; PMN; Pyrochlore; PZT

1. Introduction

PZT solid solution and Pb-based ferroelectric relaxor processes have attractively dielectric and piezoelectric constants, but they still have some disadvantages. First, a considerably high sintering temperature for Pb-based materials (about 1280 °C) is required, and the evaporation of PbO during the sintering process, makes it difficult to manufacture desired sintered products. Second, Pb-based ferroelectric relaxors are difficult to fabricate reproducibly without the appearance of a pyrochlore phase that can be detrimental to the dielectric properties. In a system containing the $Pb(Mg_{1/3}Nb_{2/3})O_3$ composition, too high sintering temperature and too long sintering time would produce a second phase owing to the vaporization of PbO. The second phase was considered as a pyrochlore phase which degraded the dielectric and piezoelectric properties of the ceramic body. The dielectric properties of polycrystalline PMN are, however, strongly influenced by ceramic processing conditions. Some steps which can be taken in order to minimize the amount of pyrochlore phase formed include (1) adding excess PbO and an optimum sintering cycle,[1] (2) using excess MgO,[2,3] (3) precalcining the PbO and Nb_2O_5 oxides (Nb_2O_5 + PbO to form $Pb_3Nb_2O_8$),[4] (4) prereacting the MgO and Nb_2O_5 oxide (Nb_2O_5 + MgO to form $MgNb_2O_6$) during the calcination step.[5,6]

Suitable addition of excess PbO not only aids in the elimination of pyrochlore phase, but also enhances densification through liquid phase sintering.[1] To meet these objectives, the low melting $4PbO{\cdot}B_2O_3$ glass was used in this study. The properties of PbO-based glasses were reported by Fajaus and Kreidl.[7] They found these glasses not only to have a low flow temperature, but also to exist a high polarizability which is helpful to the polarization of the ceramics. The melting temperature of the $4PbO{\cdot}B_2O_3$ was around 500 °C, so it would provide a liquid phase during sintering. The Pb-based relaxor compounds, such as PMN, which have considerably lower electronegative differences and lower tolerance factor, are found to be difficult to synthesize in perovskite form. Such compounds tend to form a more covalently bonded pyrochlore structure, $Pb_2Nb_2O_7$, or the anion deficient pyrochlore, $Pb_3Nb_4O_{13}$, phase. Increasing the tolerence factor and electronegativity

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difference of such compounds by the addition of Pb(Ti,Zr)O_3, is found to be highly successful in stabilizing the perovskite structure. Hence, the host system is a perovskite type piezoceramics 0.875Pb(Ti,Zr)O_3–0.125Pb $(Mg_{1/3}Nb_{2/3})O_3$. The effect of the amounts of the glass frit addition on the dielectric and piezoelectric properties of 0.875PZT–0.125PMN ceramics was discussed in this paper.

2. Experimental procedure

The ceramics used in this study are 0.875Pb(Ti,Zr)O_3–0.125Pb$(Mg_{1/3}Nb_{2/3})O_3$ and the glass frit used is $4PbO{\cdot}B_2O_3$.

For the glass formation, the raw materials used are reagent-grade PbO and B_2O_3. After mixing, the mixture was placed in an alumina crucible and melted in an electric furnace. Because PbO and B_2O_3 lost due to vaporization in the firing process, several precautions were taken to ensure compositionl accuracy. The glass melted very rapidly at 900–1000 °C and all the melts were held no longer than a total of 30 min at temperature, even for repeated meltings. Once melting was complete, the crucible was removed from the furnace and the molten glass was poured into a bucket of cold water. After drying, the glass was ground in a mortar and pestle and pressed through a 325-mesh screen.

The host $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ powders, with $0.45 \leqslant y \leqslant 0.55$, were formulated and fabricated by conventional ceramic technology with reagent-grade PbO, ZrO_2, TiO_2, MgO and Nb_2O_5. After weighting, the raw materials were mixed with acetone in an alumina ball mill for 4 h. The mixtures were dried and calcined at 850 °C for 2 h. After that, the calcined 0.875PZT–0.125PMN powders were mixed with 4PbO. B_2O_3 glass powder. The mixtures of host 0.875PZT–0.125PMN powders and glass powder were homogenized with acetone in the ball mill for 24 h. In general, the more homogeneous the additive distribution before liquid formation, the more rapid the densification during the liquid phase sintering. For this reason, it is common to mill the powders longer to increase homogeneity, reduce particle sizes and to break apart agglomerates. After drying, the mixtures were pressed into samples in the form of discs, 14 mm in diameter and 1 mm in thickness. The samples were covered with alumina crucible and fired at 1150 °C for 30 h. In order to provide a positive vapor pressure, $PbZrO_3$ with 3 wt.% excess PbO was used as the packing powder. After sintering, the sintered samples were polished and silver paste electrodes were fired on to both sides of the disk. The general poling technique was to immerse the samples in silicone oil and subject them to a high DC field by 3 kV/mm at 90 °C for 30 min. Twenty-four hours after poling, the dielectric and piezoelectric properties were measured with HP4192A LF impedance Analyzer in reference of the IRE Standards.[8]

In order to determine crystal structure, crystal system and lattice constants, the sintered ceramic samples were polished and measured at room temperature by the X-ray diffraction (XRD) method. By using the scanning electron microscope (SEM), the free surface of the sintered ceramic body was observed. The mean grain size was calculated by the line intercept method.[9] The density was measured by water displacement method.

3. Results and discussion

3.1. Dielectric and piezoelectric properties

The influence of glass frit on the properties of $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with $y = 0.45$–0.55 will be discussed. The effect of glass frit on the properties of 0.875PZT–0.125PMN ceramics is shown in Figs. 1–4. The sintering condition was chosen at 1150 °C for 30 h. In Fig. 1, the highest value of the planar coupling factor k_p is at $y = 0.5$. The 0.875PZT–0.125PMN ceramics doped with 0.2 wt.% $4PbO{\cdot}B_2O_3$ had a higher k_p value than other compositions. In Fig. 2, there is the highest value of the poled dielectric constant K_{33}^T near $y = 0.51$. The K_{33}^T of 0.875PZT–0.125PMN ceramics doped with 0.2 wt.% $4PbO{\cdot}B_2O_3$ had a larger value than other compositions. In Fig. 3, the mechanical quality factor Q_m had the lowest value at $y = 0.5$. The Q_m of 0.875PZT–0.125PMN ceramics doped with 0.2 wt.% $4PbO{\cdot}B_2O_3$ for lower Zr compositions has a

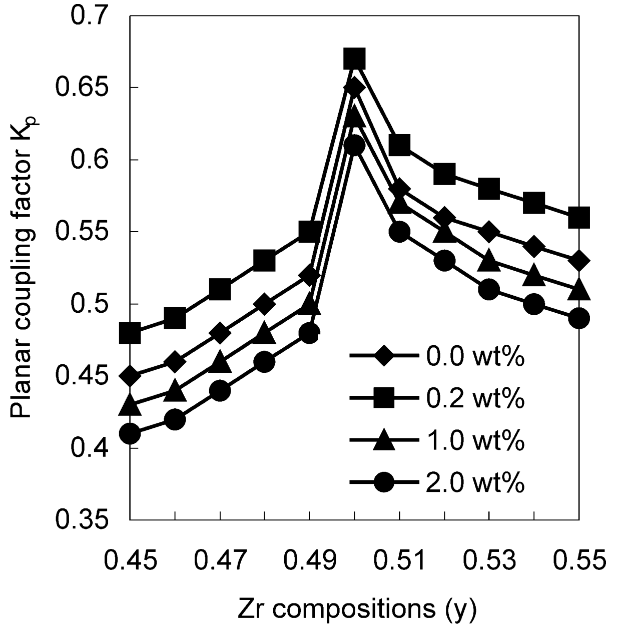

Fig. 1. Variation of the planar coupling factor of $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics as a function of Zr composition and amounts of $4PbO{\cdot}B_2O_3$ glass frit.

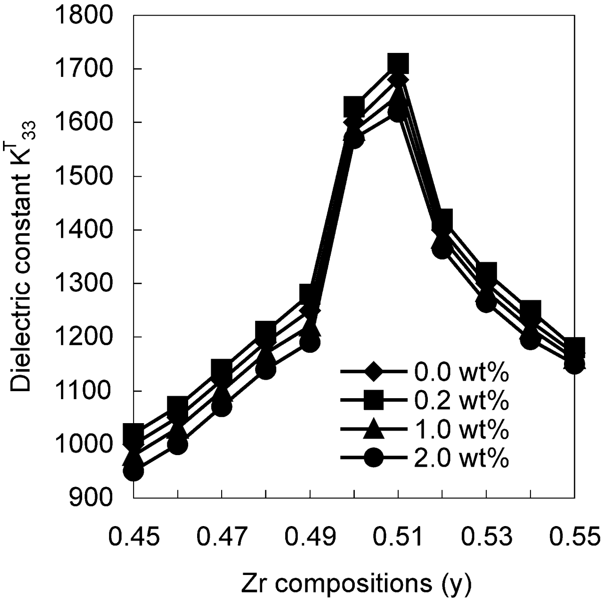

Fig. 2. Variation of the dielectric constant of $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics as a function of Zr composition and amounts of $4PbO{\cdot}B_2O_3$ glass frit.

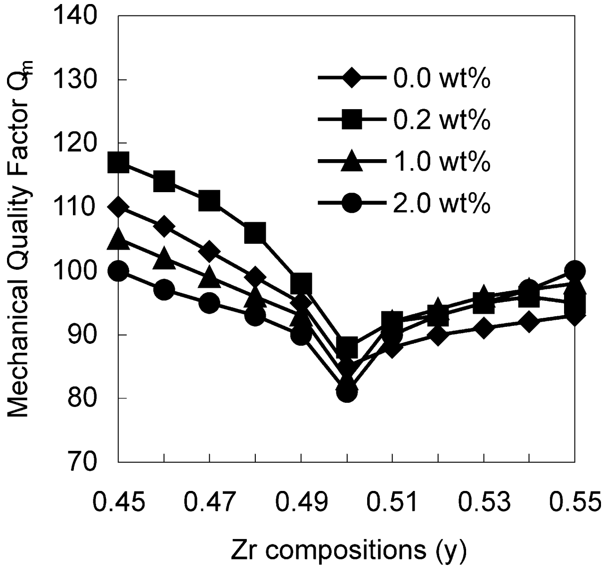

Fig. 3. Variation of the mechanical quality factor of $0.875Pb(Ti_yZr_{1-y})$ O_3–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics as a function of Zr composition and amounts of $4PbO{\cdot}B_2O_3$ glass frit.

higher value, the Q_m of those doped with 2 wt.% $4PbO{\cdot}B_2O_3$ for higher Zr compositions has a larger value. In Fig. 4, the dielectric loss tangent has a lower value for lower Zr compositions. On the other hand, the dielectric loss tangent of 0.875PZT–0.125PMN ceramics doped with 2 wt.% $4PbO{\cdot}B_2O_3$ has a lower value than other compositions. The PbO-based glasses without alkali ions have low dielectric loss tangent values.[10] Hence, the value of the dielectric loss tangent in ceramics is decreased with increasing amounts of the glass frit.

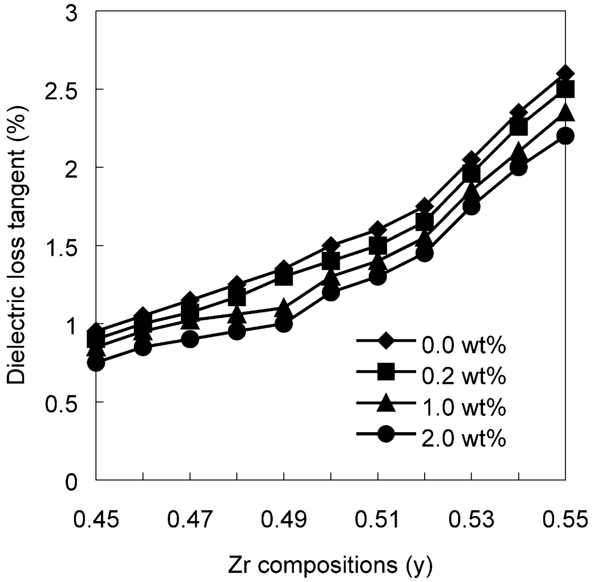

Fig. 4. Variation of the dielectric loss tangent of $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics as a function of Zr composition and amounts of $4PbO{\cdot}B_2O_3$ glass frit.

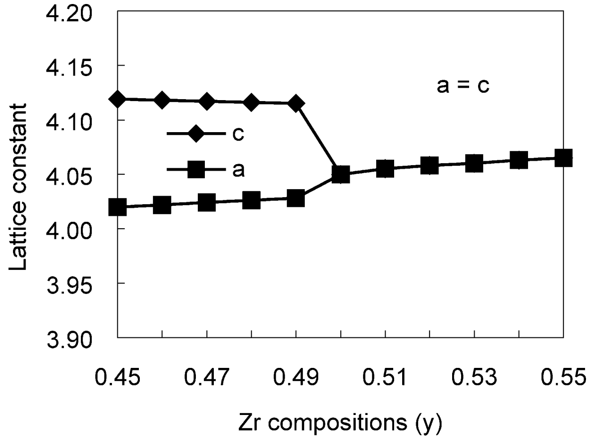

Fig. 5. Variation of the lattice constant of the $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different y values at room temperature.

4. XRD analysis

Fig. 5 shows the lattice constant of $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different y values at room temperatures. The perovskite appears to have the rhombohedral symmetry for $y>0.5$, and the tetragonal symmetry for $y<0.5$. Fig. 6 shows the XRD patterns of $0.875Pb(Ti_{0.5}Zr_{0.5})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic with different doping (0.0, 0.2, 1.0 and 2.0 wt.%) after sintering at 1150 °C for 30 h. The volume fraction of the pyrochlore phase is calculated from the XRD of each sample by means of the relative intensities of the (222) pyrochlore peak I_{pyro} (i.e. at 29.2° of Fig. 6) and the (110) perovskite peak I_{perov} (i.e. at 30.9° of Fig. 6) using the formula:

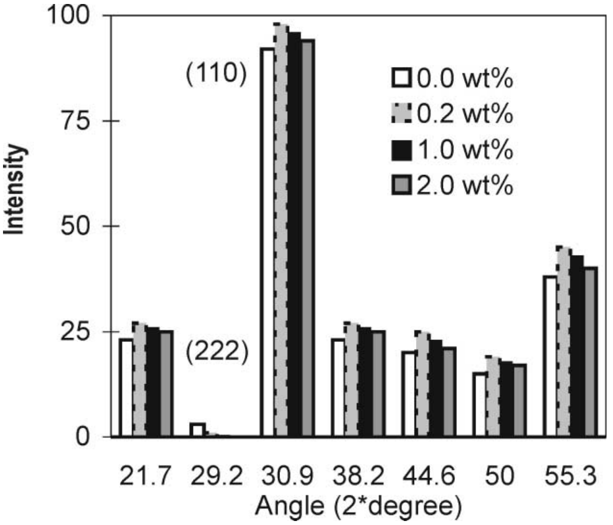

Fig. 6. The XRD patterns of $0.875Pb(Ti_{0.5}Zr_{0.5})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ doped with different doping [(a) 0.0 wt.%, (b) 0.2 wt.%, (c) 1.0 wt.% and (d) 2.0 wt.%, respectively] after sintering at 1150 °C for 30 h.

$$\text{Volume fraction of pyrochlore} = \frac{I_{\text{pyro}}}{I_{\text{pyro}} + I_{\text{perov}}}$$

It was thus determined that the system doped with 0.0, 0.2, 1.0 and 2 wt.% $4PbO{\cdot}B_2O_3$ contained 3.0, 1.0, 0.2 and 0.0% of the pyrochlore phase, respectively. The justification for the use of the expression is that, despite its simplicity, it gives very close agreement with values obtained using rigorous, quantitative X-ray analysis methods. It is evident, therefore, that an addition of excess PbO ($4PbO{\cdot}B_2O_3$) enhances the reaction rate and allows the formation of the perovskite phase. Thus the overall reaction sequences observed by the XRD analysis can be represented by the following equations:

$$\begin{aligned} &PbO + 7/16ZrO_2 + 7/16TiO_2 + 1/24MgO \\ &\quad + 1/24Nb_2O_5 \rightarrow 7/8Pb(Ti_{0.5}Zr_{0.5})O_3 \\ &\quad + 1/8Pb(Mg_{1/3}Nb_{2/3})O_3 \end{aligned} \tag{1}$$

$$\begin{aligned} &7/8Pb(Ti_{0.5}Zr_{0.5})O_3 + 1/8Pb(Mg_{1/3}Nb_{2/3})O_3 \rightarrow \\ &7/8Pb(Ti_{0.5}Zr_{0.5})O_3 + 1/48Pb_3Nb_4O_{13} + 1/16PbO \\ &+ 1/24MgO \end{aligned} \tag{2}$$

In the $Pb(Mg_{1/3}Nb_{2/3})O_3$ system, thermal evolution is up to 830 °C. From 830 °C up to sintering temperature (1150 °C), the formation of the perovskite phase occurs. As expected from reaction sequences (1), processes that reduce the volatility of PbO, such as shorter sintering times and closed crucible firings, lead to a complete amount of perovskite phase. Conversely, processes that lead to PbO loss, as in longer sintering times, lead to an increased amount of pyrochlore phase ($Pb_3Nb_4O_{13}$), as is evident from the reaction sequence (2). Use of the correct amounts of excess PbO essentially prevent the formation of a $Pb_3Nb_4O_{13}$ phase and, moreover, the growth of liquid phase ($4PbO.B_2O_3$) during sintering should probably increase the kinetics of the reaction, as expected from the reaction sequence (1).

4.1. SEM observations

The scanning electron micrograph of a fracture surface of the $0.875Pb(Ti_{0.5}Zr_{0.5})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic with different $4PbO.B_2O_3$ doping obtained after sintering at 1150 °C for 30 h is shown in Fig. 7. On formation of a liquid phase, there is a rearrangement of particles to give a more effective packing. The driving force for densification is derived from the capillary pressure of the liquid phase located between the fine solid particles. There is during the sintering process a solution of small particles and growth of larger particles of material transfer through the liquid phase. The ceramic doped with 0.2 wt.% $4PbO{\cdot}B_2O_3$ has less porosity and is more dense than that without doping. With higher doping (i.e. 1 and 2 wt.%), the glassy phase is segregated at the grain boundary. The remaining glassy phase is detrimental to the properties of the ceramics. The volume of glassy phase increases for increasing amounts of dopant.

4.2. Grain growth mechanism

For the purpose of studying the influence of the grain size, the $0.875Pb(Ti_{0.5}Zr_{0.5})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic is sintered at different conditions. For 0.875 PZT–0.125PMN ceramic, the kinetics of grain growth give the mean grain size versus time as follows:[11]

$$R^n = k \times t \tag{3}$$

where R is the mean grain size, t is time, k is rate constant, and n is the grain growth kinetic exponent. Eq. (3) can be described in the following form: $n(\log R) = \log k + \log t$. The relationships between the grain size $\log(R)$ and sintering time $\log(t)$ are shown in Fig. 8. The grain growth kinetic exponent n can be determined from the inverse of the slope of the $\log(R)-\log(t)$ relation and is near to 2.8 for the composition without $4PbO{\cdot}B_2O_3$ doping, 2.5 for the composition adding 0.2 wt.% $4PbO{\cdot}B_2O_3$ doping, 2.6 for the composition adding 1 wt.% $4PbO{\cdot}B_2O_3$ doping and 2.7 for those adding 2 wt.% $4PbO{\cdot}B_2O_3$. It is inferred from Eq. (3) as follows:

$$\frac{d\log(R)}{d\log(t)} = \frac{1}{n} \tag{4}$$

so that the grain growth rate $d\log(R)/d\log(t)$ decreases, causing the grain growth kinetic exponent n to increase. The grain sizes of $0.875Pb(Ti_{0.5}Zr_{0.5})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic doped with 0.2 wt.% glass frit are larger than with 2 wt.% glass frit, causing the n parameter to

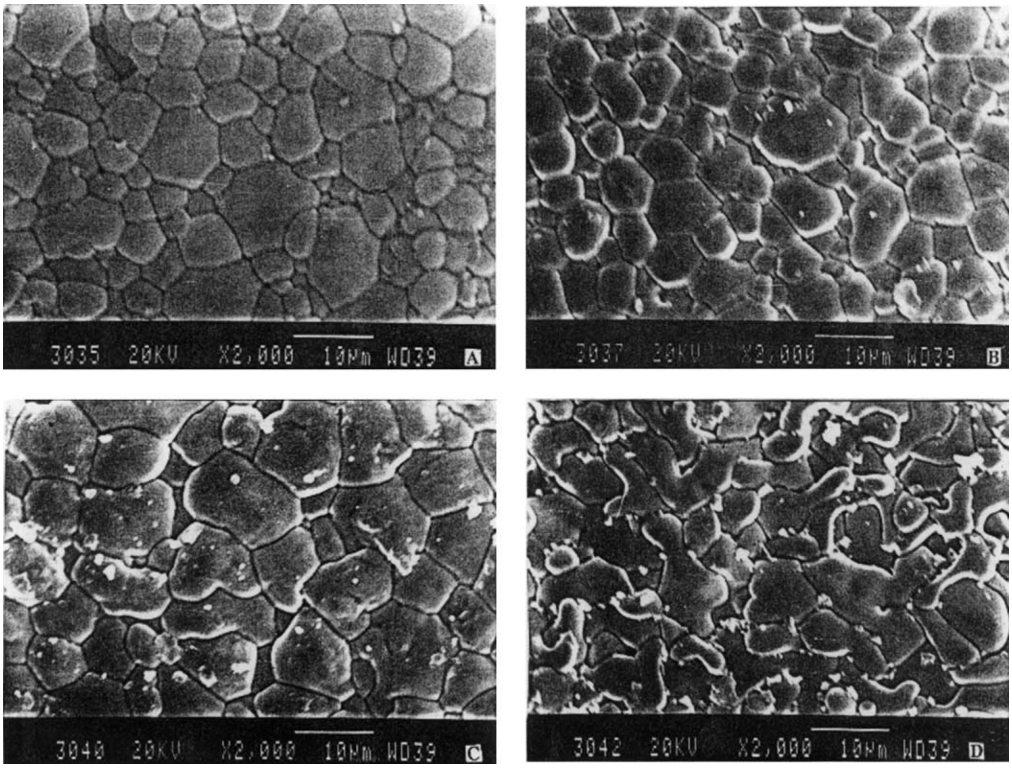

Fig. 7. The microstructure of $0.875Pb(Ti_{0.5}Zr_{0.5})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different $4PbO{\cdot}B_2O_3$ doping [(a) 0.0 wt.%, (b) 0.2 wt.%, (c) 1.0 wt.% and (d) 2.0 wt.%] after sintering at 1150 °C for 30 h.

increase from 2.5 to 2.7. Alternatively, ceramic without doping have smaller grain sizes than that doped with 0.2 wt.% glass frit, causing the n parameter to decrease from 2.8 to 2.5 as shown in Fig. 8.

5. Discussions

To evaluate the effect of $4PbO{\cdot}B_2O_3$ doping on the characteristics, the substituting and interstitial process of additive ions must be taken into account. There may be A- or B-site substitution and the possibility of either octahedral or tetrahedral insterstitial packing by doping into an ABO_3 perovskite structure. Which effect is dominant will depend on the radius of the doping ion and its chemical properties, such as valence and electronegativity. It is presumed that Pb^{+2} has an A-site occupation, where B^{+3} undergoes B-site substitution. There is some probability of octahedral and tetragonal interstitial occupation for B^{+3}. If the small ion has interstitial occupation, polarizing treatment creates a slight shift of B^{+3} relative to its position before polarizing. A higher dipole moment contributes an increase of K_{33}^{T}. According to the rules of Goldschmidt, the dopant cation enter into the sites (A or B) in the ABO_3 perovskite structure if the ion and the substituted ion radii do not differ by more than 15%. The effect may enhance the interstitial doping of B^{+3} because of its rather smaller radii (0.2 Å) compared with Zr^{+4} (0.87 Å), Ti^{+4} (0.64 Å) and Nb^{+5} (0.69 Å). It is therefore believed that B^{+3} doping mostly has an interstitial occupation rather than a substitution at B-site. However, high concentrations of B^{+3} interstitials were unlikely in the close-packed perovskite structure with a small rattling space. Beyond the solubility limit, the second phase appears gradually and the dielectric constant decreases. It is believed that the glassy phase effect the dielectric and piezoelectric properties.

From the XRD patterns, $0.875Pb(Ti_yZr_{1-y})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics have rhombohedral symmetry for $y > 0.5$, and tetragonal symmetry for $y < 0.5$. It means the morphotropic phase (MPB) between the rhombohedral and the tetragonal phase of compositions is at $y \approx 0.5$ in this system. Near the MPB the solid solutions have the best electromechanical properties. As small amounts of $4PbO{\cdot}B_2O_3$ dopant (i.e. 0.2 wt.%) are added to the 0.875PZT–0.125PMN ceramics, it can depress the amount of the pyrochlore phase and increase the value of K_{33}^{T} and Q_m. On the other hand, it is interesting to notice that ceramic doped with 0.2 wt.% glass frit had higher K_{33}^{T} value and better piezoelectric properties despite the presence (1 vol.%) of a pyrochlore phase. Pyrochlore has previously been considered to be detrimental to the dielectric properties of PMN ceramics. The higher doping materials (1 and 2 wt.%) studied here, however, contained less pyrochlore than ceramic doped with 0.2-wt.% glass frit, yet the former had a much lower dielectric constant. This implies that the

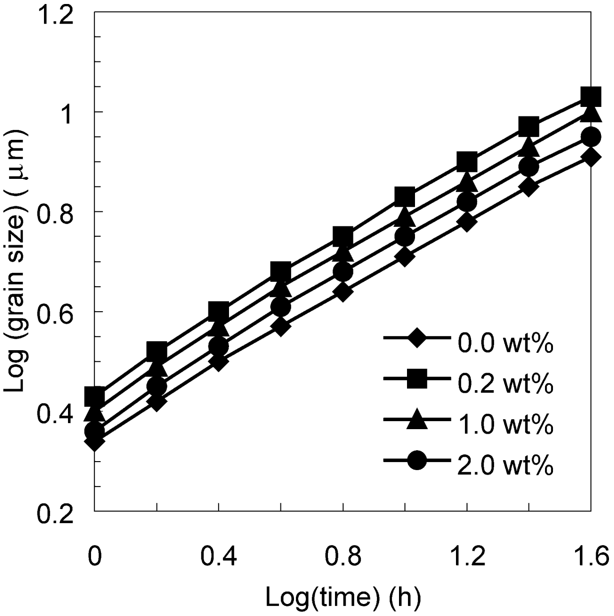

Fig. 8. The relations between sintering time log(t) and grain size log(R) of $0.875Pb(Ti_{0.5}Zr_{0.5})O_3$–$0.125Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics with different $4PbO{\cdot}B_2O_3$ doping conditions (without doping, 0.2, 1.0 and 2.0 wt.%). The sintering temperature is always fixed at 1150 °C.

pyrochlore phase is not, directly at least, all that detrimental to the dielectric constant. For higher doping materials, the glassy phase, which interferes with the poling behavior and reduces the properties of k_p and K_{33}^T, is segregated at the grain boundary. As for the mechanical quality factor, it was involved in domain wall loss. The friction between domain walls was increased with increasing amounts of the glassy phase, and consequently, the Q_m was decreased.

Grain growth in 0.875PZT–0.125PMN ceramics with sintering time and amounts of $4PbO{\cdot}B_2O_3$ dopants, was studied. The grain growth kinetic exponent, n, has an inverse relation with the rate of grain growth. The low-melting $4PbO{\cdot}B_2O_3$ frit formed a liquid phase that promoted grain growth and densification by solution-precipitation, capillary force and rearrangement during the early and middle stages of sintering. This results in an increase of grain growth rate and a decrease of grain growth kinetic exponent. Addition of a glassy phase as an excess $4PbO{\cdot}B_2O_3$ above the solubility limit results in a decrease of grain growth rate and a increase of grain growth kinetic exponent.

6. Conclusions

The $4PbO{\cdot}B_2O_3$ doping has a number of advantages over the non-doped 0.875PZT–0.125PMN system. Because the $4PbO{\cdot}B_2O_3$ additive can form a liquid phase to promote densification during sintering, and the $4PbO{\cdot}B_2O_3$ doping can compensate the volatility of the PbO during sintering and depress the amounts of the pyrochlore phase. As small amounts of $4PbO{\cdot}B_2O_3$ dopant (i.e. 0.2 wt.%) are added to the 0.875PZT–0.125PMN ceramics, they can depress the amounts of the pyrochlore phase and increase the value of k_p, K_{33}^T and Q_m. Depending on the doping amount, the $4PbO{\cdot}B_2O_3$ appears not only to be a grain growth promoter within the solubility limit, but also to be a grain growth inhibitor above the solubility limit. With suitable doping concentration and sintering temperature, a dense microstructure was obtained. The value of the k_p, K_{33}^T and Q_m is increased and dielectric loss tangent is decreased when small amounts of $4PbO{\cdot}B_2O_3$ dopant (i.e. 0.2 wt.%) are added to the 0.875PZT–0.125PMN ceramics. With more $4PbO.B_2O_3$ doping (i.e. 2 wt.%), the value of the k_p and K_{33}^T is decreased due to the glassy phase segregation at the grain boundary.

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