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Effects of $30B_2O_3$–$25Bi_2O_3$–45CdO glass addition on the sintering of $12Pb(Ni_{1/3}\ Sb_{2/3})O_3$–$40PbZrO_3$–$48PbTiO_3$ piezoelectric ceramics

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Abstract

Effects of $30B_2O_3$–$25Bi_2O_3$–45CdO (BBC for short) glass addition on the sintering of $12Pb(Ni_{1/3}Sb_{2/3})O_3$–$40PbZrO_3$–$48PbTiO_3$ (12PNS–40PZ–48PT) piezoelectric ceramics have been investigated using PbO, ZrO_2, TiO_2, NiO, Sb_2O_3, B_2O_3, Bi_2O_3 and CdO powders as starting materials. Using calcined 12PNS–40PZ–48PT powders with BBC glass concentration from 1.0 to 5.0 wt.% and sintering at 925°C for 2 h, the X-ray diffraction patterns show that the addition of 1.0 wt.% BBC glass results in 100% tetragonal when compared with 2.0–5.0 wt.% BBC glass addition which causes the coexistence of both tetragonal and rhombohedral phases. On the other hand, when sintered at 950°C for 2 h, for the addition of 1.0 wt.% BBC glass the crystalline phase appears to be largely reombohedral, and an increased tendency for the evidence of the parasitic phase of pyrochlore for the addition of 2.0–5.0 wt.% BBC glass. The sintering temperature of a 12PNS–40PZ–48PT piezoelectric ceramic can be reduced lower than 1000°C by the addition of 1.0–5.0 wt.% BBC glass and a density of 97.5% of the theoretical is obtained for the compact containing 2.0 wt.% BBC glass when sintered at 925°C for 2 h. After sintering at 925°C for 2 h, the planar coupling coefficient (K_p) value decreases from 0.51 to 0.30 as the of BBC glass concentration increases from 2.0 to 5.0 wt.%. The mechanical quality coefficient (Q_m) increases as the BBC glass concentration increases from 2.0 to 4.0 wt.%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pb(Ni, Sb)O_3; $PbTiO_3$; $PbZrO_3$; Perovskites; Piezoelectric properties; Sintering

1. Introduction

Lead zirconate-titanate (PZT) ceramics are used extensively for piezoelectric devices and are promising materials for electrooptic and information storage devices. These applications require very precisely controlled piezoelectric properties; hence, close control of ceramic microstructure and composition is required.[1] The understanding of certain physical phenomena in piezoelectric ceramics has developed continuously during the last few decades and presently it is possible to discuss in some details the physics of piezoelectric ceramics.[2] Shirane et al.[3,4] studied lead zirconate-lead titanate solid solutions and found a morphotropic phase transition. The crystal structure changed from tetragonal to rhomobhedral in the vicinity of Zr/Ti = 53/47 corresponding to a composition of the morphotropic phase boundary.[5] Jaffe et al.[6] found excellent piezoelectric properties as well in the composition $Pb(Zr_{0.55}\ Ti_{0.45})O_3$ near the morphotropic phase boundary.

Ouchi et al.[7] also pointed out that the $Pb(Mg_{1/3}\ Nb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ system, with compositions between tetragonal and pseudocubic or rhombohedral phases (near the morphotropic phase boundary) formed a solid solution of the perovskite structure, having a high planar coupling coefficient. Although it possesses a high potential as an electromechanical transducing material, the mechanical quality factor is too low to permit their use as a resonator in filter circuits.[7] High mechanical quality factor and planar coupling coefficient are desirable for transducers in phonograph pickups and in ultrasonic vibrations. Many researchers have reported the effect of additions on the piezoelectric properties of the system $PbZrO_3$–$PbTiO_3$.[8–12]

In this work the PZT ceramics were prepared by the mixed-oxide technique. In the conventional sintering of PZT ceramics, control of the atmosphere and sintering temperature is critical due to the evaporation of PbO.[13] The volatility of PbO in PZT ceramics during sintering has histrorically been a stumbling block to the reproducible production of high-quality piezoelectric ceramics. Thus,

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an improved multiphase packing powder technique and/or pellets containing excess PbO and $PbZrO_3$ or a PbO–$PbZrO_3$ mixture were used to provide a positive vapor pressure. Surrounding the PZT ceramics with packing powders during sintering allows the reproducible processing of PZT composition to a constant stoichiometry.[1,14,15] The sintering temperature of conventional PZT piezoelectric ceramics vanes from about 1200 to 1350°C. This high sintering temperature requires the use of precious metals for internal electrodes in multilayer piezoelectric devices.[16]

The development of low-temperature sintering piezoelectric ceramics reduces energy consumption and environmental pollution and enables the ceramics to be cofired with less-expensive metals in multilayer devices.[16] In general, the sintering temperature can be reduced by doping with low melting oxides or glasses. Wittmer and Buchanan[17] have reported that the addition of 0.10–6.0 wt.% V_2O_5 to PZT ceramics promoted rapid densification below 975°C, thereby reducing the need for PbO atmosphere control. On the other hand, previous experiments have shown that the properties of low-temperature sintering piezoelectric ceramics are degraded.[16,18,19]

The present work was undertaken to investigate the effect of $30B_2O_3$–$25Bi_2O_3$–45CdO (mol%; BBC) glass with 1.0 wt.% excess PbO addition on the sintering of $12Pb(Ni_{1/3}Sb_{2/3})O_3$–$40PbZrO_3$–$48PbTiO_3$ (12PNS–40PZ–48PT) piezoelectric ceramics. The object of this study was to reduce the sintering temperatures of 12PNS–40PZ–48PT ceramics and eliminate the need for a controlled PbO atmosphere, while maintaining desirable piezoelectric properties. To limit the scope of this paper, three aspects of this investigation were described as follows: (i) to present the phase stability and compare that with the addition of BBC glass and sintering temperature at the same time; (ii) to evaluate the relationship between density, BBC glass concentration, and sintering temperature; (iii) to evaluate the relationship between planar coupling coefficient (K_p) and mechanical quality coefficient (Q_m) and various BBC glass concentration and sintering temperatures.

2. Experimental procedure

2.1. 12PNS–40PZ–48PT piezoelectric ceramics preparation

The base composition of this study was $Pb(Ni_{1/3}Sb_{2/3})O_3 = 12$ mol%, $PbZrO_3 = 40$ mol% and $PbTiO_3 = 48$ mol%. The low-melting-temperature frit consisted of $B_2O_3 = 30$ mol%, $Bi_2O_3 = 25$ mol% and $CdO = 45$ mol%. 1.0 wt.% excess PbO and low-melting-temperature frit were added to the host 12PNS–40PZ–48PT ceramic powder in concentration varying from 1.0 to 5.0 wt.%.

The 12PNS–40PZ–48PT ceramic powders were prepared by the mixed-oxide technique. The low-melting-temperature BBC frit was added after calcining. The flow chart for the preparation of 12PNS–40PZ–48PT calcined powders with BBC frit is shown in Fig. 1.

The raw materials of PbO (purity >98%, supplied by Santoku Chemical Co. Ltd, Japan), TiO_2 (purity >99%, supplied by MERCK, Germany), ZrO_2 (purity >99.9%, supplied by Showa Chemicals Inc., Japan), NiO (purity >99.9%, supplied by FERAK, Germany) and Sb_2O_3 (purity >99.9%, supplied by FERAK, Germany) were weighed and mixed. Each mixture of the starting powders was milled and mixed in a centrifugal mill, followed by wet-homogenization with distilled water for 8 h using high purity Al_2O_3 balls (SSA-S standard 99.5%, diameter 1.0 cm). The obtained powders were dried in an oven and subsequently mixed and dried in a covered alumina crucible (SSA-S standard) and finally calcined at 850°C for 8 h with a heating and cooling rate of $350°C \cdot h^{-1}$. The calcined powders were reground using wet ball-milling for 15 min, then dried and sifted.

The starting materials used for preparing the low-melting-temperature BBC glass were of the following analytical grade: B_2O_3 (purity >99%, supplied by MERCK,

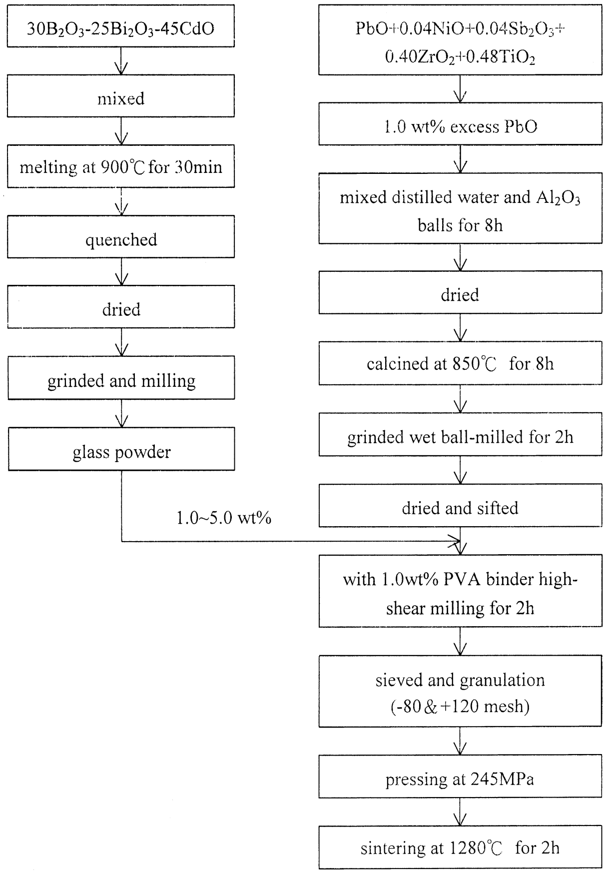

Fig. 1. The flow chart of preparing 12PNS–40PZ–48PT calcined powders with BBC glass content.

Germany), Bi_2O_3 (purity >99%, supplied by FERAK, Germany) and CdO (purity >99.99%, supplied by Streem Chemicals, USA). All samples were obtained in 40–50 g batches by melting in a platinum crucible at 900°C in an electric furnace for 30 min. After homogenizing, the melt was quenched in water, dried, crushed and grinded.

The fine calcined powders were mechanically blended with 1.0–5.0 wt.% BBC glass powders and a 1.0 wt.% PVA binder in a high-shear mill for 2 h and sieved after granulation. After granalation the powder mixture was isostatically pressed at 245 MPa into a pellet of 1.5 mm in height and 12.0 mm in diameter.

Finally, the pellets were put in a sealed alumina crucible and sintered between 900 and 975°C for 2 h with a heating rate of $4°C\cdot min^{-1}$.[20] The sintered pellet was lapped to a thickness of 1.00 mm. An electrode was made by painting with silver paste and firing at 780°C for 20 min.

2.2. Analysis

After sintering, the bulk density of all samples was measured using the Archimedes method.

$$\text{Bulk density} = D(W - S)^{-1}(\text{g}\cdot\text{cm}^{-3}) \tag{1}$$

where

D = weight of a dried sample in air,
S = weight of a sample in water,
W = weight of a wet sample in air.

The phase structure was identified by X-ray diffraction (XRD) analysis. The XRD work was performed with a Rigaku X-ray diffractometer with Cu K_α radiation and a Ni filter at a scanning rate (2θ) of $0.25°\cdot min^{-1}$ (Model Kad IIA, Rigaku, Tokyo, Japan).

The fracture surface of the sintered specimens was examined by scanning electron microscope (SEM, JEOL 840, Tokyo, Japan).

Preceding the piezoelectric measurements, the pellets were poled in silicone oil at 100°C by applying a static field of 3.5 $kVmin^{-1}$ for 1 h. The pellets were field-cooled to room temperature in 30 min. Twenty-four hours after poling, the values of K_p[21] and Q_m[22] were calculated from the following equations, respectively.

$$K_p = [2.51(f_a - f_r)f_r^{-1}]^{1/2} \tag{2}$$

and

$$Q_m = f_a^2[2\pi R_f C f_r(f_a^2 - f_r^2)]^{-1} \tag{3}$$

where f_a = antiresonant frequency (Hz), f_r = resonant frequency (Hz), R_r = resonant impedance (ohms), C = electrical capacitance (farads).

3. Results and discussion

3.1. Crystalline phase of the 12PNS–40PZ–48PT piezoelectric ceramics with BBC additive

In the present study, the base composition of PNS: 12 mol%, PZ = 40 mol% and PT = 48 mol% was at the morphotropic phase boundary in the xPNS–(52-x)PZ–48PT ($4 \leqslant x \leqslant 14$) and 12PNS–(88-$y$)PZ–$y$PT ($44 \leqslant y \leqslant 52$) piezoelectric ceramics system.[23] The typical XRD patterns of the 12PNS–40PZ–48PT piezoelectric ceramics added with various BBC glass concentration and sintered at 925°C for 2 h are shown in Fig. 2. It indicates that the addition of 1.0 wt.% BBC glass results in 100% tetragonal when compared with 2.0–5.0 wt.% BBC glass addition which causes the coexistence of both tetragonal (F_T) and rhombohedral (F_R) phases as revealed by the splitting of the (2 0 0) peak reflection in into $(002)_T$ and $(200)_R$. The reflection indexed with T is assigned to the tetragonal piezoelectric phase, F_T, whereas that indexed with R to the rhombohedral piezoelectric phase, F_R. Fig. 2 illustrates the phase transformation from F_T to F_R. This result corresponds to the report of Lucuta et al.,[13] Ari-Gur and Benquigi,[24] and Hank et al.[25] In the present investigation, by adding various concentrations of BBC glass to 12PNS–40PZ–48PT specimens, the coexistence of both ferroelectric phase at the morphotropic phase boundary has been changed.

Fig. 2 also indicates that, in these samples, as the BBC glass concentration increased from 4.0 to 5.0 wt.%, the piezoelectric perovskite structure is often associated

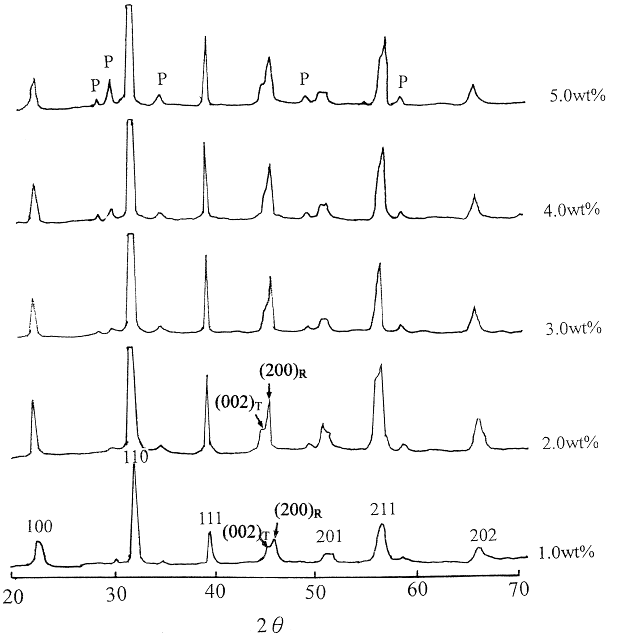

Fig. 2. XRD patterns of 12PNS–40PZ–48PT piezoelectric ceramic added with various BBC glass concentrations and sintered at 925°C for 2 h.

with the parasitic phase of pyrochlore. The formation of the pyrochlore phase is due to the excese liquid phase in composition containing beyond 3.0 wt.% BBC glass.

Typical XRD patterns of the specimens sintered at 950°C for 2 h is shown in Fig. 3. It indicates that, in general, for the addition of 1.0 wt.% BBC glass, the crystalline phase appears to be largely rhombohedral as compried with Fig. 2. On the other hand, there was an increased tendency for the evidence of the parasitic phase of pyrochlore during the addition of BBC glass concentration from 2.0 to 5.0 wt.%. According to Figs. 2 and 3, when the specimens of the same composition are sintered at 950°C for 2 h, the intensity of parasite phase is greater than that at 925°C for the same sintering time. Hence the crystalline phases obtained from these sintered samples are clearly composed of the mixed solid solutions with different mixing ratios over the temperature range examined in the sintering study.

3.2. Bulk density of the sintered samples

The effect of BCC glass concentration on the bulk density for the specimens sintered at various temperatures for 2 h is shown in Fig. 4. It indicates that, with the specimens containing 1.0 wt.% BCC glass, the bulk density increases from 7.36 (92.0% of theoretical) to 7.54 g·cm^{-3} (94.2% of theoretical) for an increase in sintering temperature from 900 to 975°C. This result is attributed to an increase in the number of liquid phase clusters per unit grain boundary area with increasing sintering temperature due to increased diffusion. With only 1.0 wt.% BBC glass addition, there are insufficient liquid amount and poor wetting of the grain boundaries. In the liquid phase sintering, the formation of poor wetting liquid may lead to swelling of the compact during heating without densification,[26] hence the bulk density attained is below 7.60 g·cm^{-3} ($<$95.2% of theoretical).

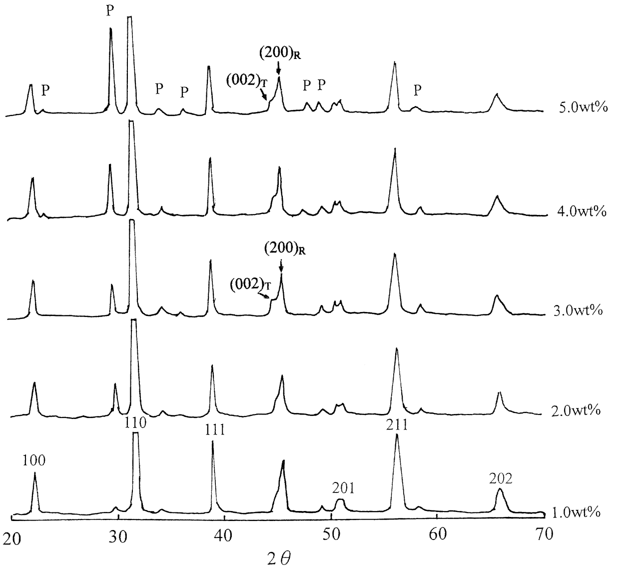

Fig. 3. XRD patterns of 12PNS–40PZ–48PT piezoelectric ceramic added with various BBC glass concentrations and sintered at 950°C for 2 h.

Fig. 4 also indicates that a critical BBC glass concentration occurs, providing an increase in bulk density. In addition, the maximum bulk density of 7.86 g·cm^{-3} is obtained for the specimens containing 2.0 wt.% BBC glass when sintered at 975°C for 2 h. As the BBC glass concentration is increased beyond 2.0 wt.%, the bulk density decreases with increasing BBC glass concentration. The decrease in density with increased BBC glass concentration ($>$2.0 wt.%) is attributed to the formation of a lower density second phase. Excess liquid phase is found in the composition containing greater than 3.0 wt.% BBC glass.

From Fig. 4, it is found that the relationship between sintering temperature and BBC glass concentration indicates the lowest temperature required for the production of the sintered specimen having a desired BBC glass concentration and a bulk density more than 95% of the theoretical (T.D. = 8.0 g·cm^{-3}). For the specimens containing 2.0 wt.% BBC glass and sintered at 925 and 975°C, the highest densities are 7.80 g·cm^{-3} (97.5% of the theoretical) and 7.86 g·cm^{-3} (98.2% of theoretical), respectively. This result seems to be very useful for the fabrication of low-temperature sintering piezoelectrics with a given composition and microstructure.

3.3. K_p *and* Q_m *values of the sintered samples*

The relationship between K_p and BBC glass concentration is shown in Fig. 5. It indicates that, in general, when the sintering temperature is lower than 950°C the sintered sample has a lower K_p value (below 0.35). However, when the compact is sintered at 975°C for 2 h, the K_p value decreases from 0.48 to 0.30 as the BBC glass concentration increases from 1.0 to 5.0 wt.%. When the

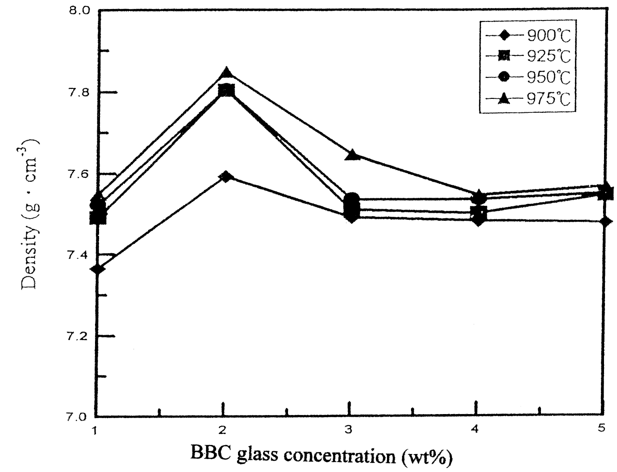

Fig. 4. Effect of BBC glass concentration on the bulk density of the base composition 12PNS–40PZ–48PT sintered at various temperatures for 2 h.

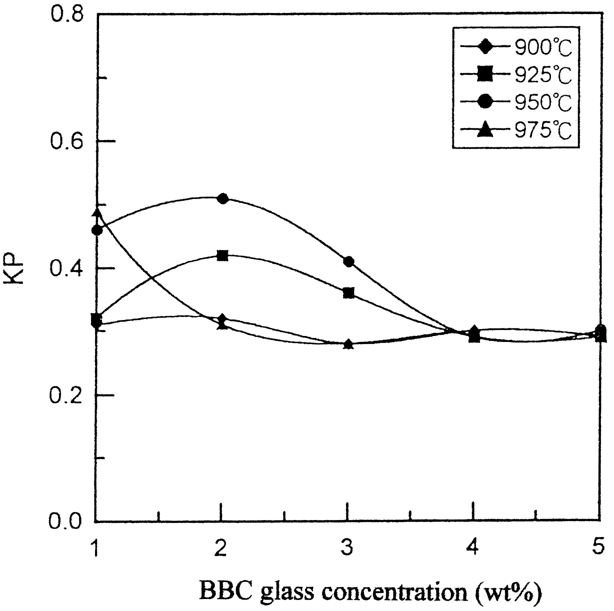

Fig. 5. The relation between K_p and addition of BBC glass concentration for on the base composition 12PNS–40PZ–48PT sintered at various temperatures for 2 h.

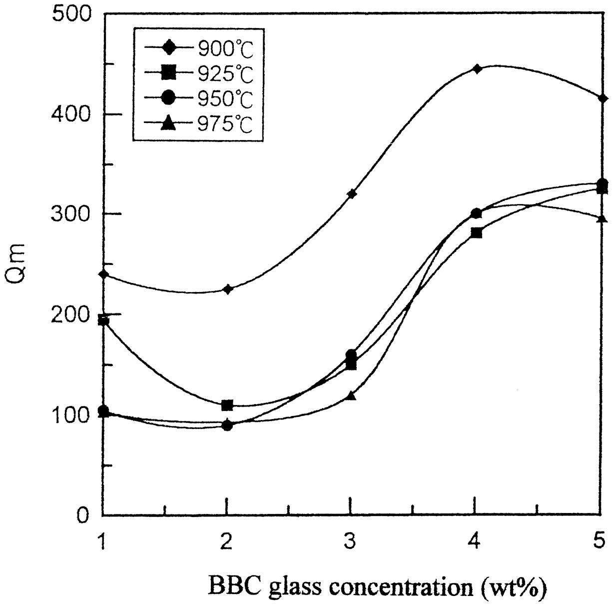

Fig. 6. The relationship between Q_m and BBC glass concentration on the base composition 12PNS–40PZ–48PT sintered at various temperatures for 2 h.

compact is sintered at 950°C for 2 h, the K_p value increases from 0.48 to 0.51 with a BBC glass concentration between 1.0 and 2.0 wt.%. On the other hand, the K_p value decreases from 0.51 to 0.30 as the BBC glass concentration increases from 2.0 to 5.0 wt.%. A cause for the lower K_p value in PZT ceramics is formation the second phase. In the present study, these results take place due to the excess liquid phase, generally leading to the growth of the parasitic pyrochlore phase.

The Pb^{2+} replacement combined with other additives such as CdO forms a low-melting-temperature liquid phase, which can promote the densification and sintering. Perhaps this is the main reason that 12PNS–40PZ–48PT ceramics with 1.0 to 5.0 wt.% BBC glass concentration can be sintered at temperatures between 925 and 975°C. If the sintering temperature is not high enough (i.e. 900°C), most ions in BBC glass still stay at the grain boundaries or grain surfaces and promote the densification. However, the substitution effects is not obvious and hence the sintered sample has a lower K_p value.

The relation between Q_m and BBC glass concentration is shown in Fig. 6. It indicates that the Q_m value increases as the BBC glass concentration increases from 2.0 to 4.0 wt.%. This result is caused by the increase of BBC glass concentration, leading to increased impurity ions and lattice defects. Thus, one can expect that the internal bias field prohibits domain wall motion at room temperature under a small electric signal which is used for the Q_m-measurement. This is probably the cause of the high Q_m value.[10] When the BBC glass concentration is greater than 4.0 wt.%, the Q_m value decreases due to the increasing amount of the pyrochlore phase for various sintering temperatures.

In the present study, for the 12PNS–40PZ–48PT with 4.0 wt.% BBC glass concentration, the Q_m value attains the maximum, 460. This value is higher than that of the base composition (i.e. 12PNS–40PZ–48PT) sintered at 1280°C for 2 h ($Q_m = 300$)[23] and that with 3.0 wt.% excess PbO content sintered at 1280°C for 2 h ($Q_m = 314$).[27]

In piezoelectric ceramics, mechanical loss, Q_m^{-1}, is mainly due to dielectric loss, tan δ, so Q_m is linearly related to tan δ through electromechanical coupling.[28] Ouchi et al.[9] also have pointed out that compositions at the morphotropic boundary yields the highest K_p, the highest dielectric constant, the lowest Q_m, and resonant impedance. Figs. 5 and 6 indicate that a minimum Q_m along with a highest K_p is obtained for the base composition (i.e. 12PNS–40PZ–48PT) with 2.0 wt.% BBC glass when sintered at 950°C for 2 h.

Since ceramic filters are made solely of piezoelectric ceramics, whose Q_m value directly determine their guality.[29,30] In the present study, they are suitable for filters used in consumer electronics.

3.4. Microstructure of the sintered samples

The progressive development of the microstructure of the 12PNS–40PZ–48PT ceramic added with 2.0 wt.% BBC glass and sintered at various temperatures for 2 h is shown in Fig. 7. Fig. 7(a) shows the particles rearrangement and formation of a liquid phase. Fig. 7(b) shows that the grains have grown and become uniform

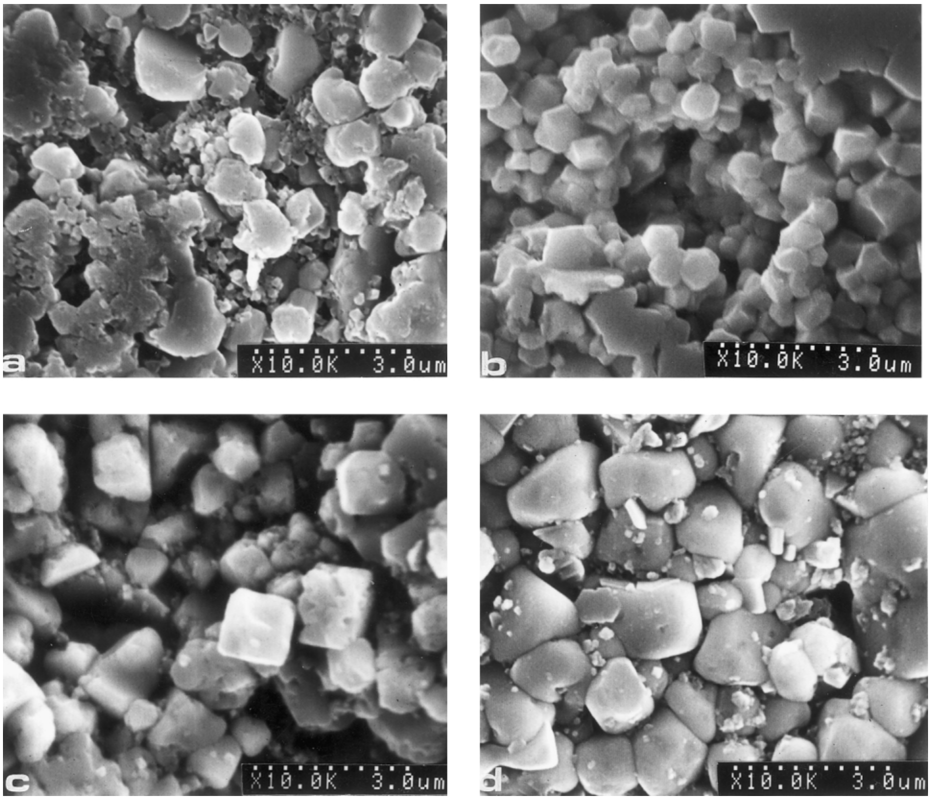

Fig. 7. The SEM micrographs of 12 PNS–40PZ–48PT piezoelectric powder added with 2.0 wt.% BBC glass and sintered at various temperatures for 2 h: (a) 900°C, (b) 925°C, (C) 950°C and (d) 975°C.

through the material transfer in a liquid phase. Fig. 7(c) shows that, the majority of the liquid phase has precipitated out, the grain shape has changed, and the grain size has increased. Fig. 7(d) shows that a dense, uniform microstructure with clear boundaries is obtained.

The sample sintered at 950°C shows wider grain boundary (Fig. 7c), but that sintered at 975°C (Fig. 7d) shows that some liquid phase remain at the grain boundaries and most of the liquid phase are absorbed by the grains.

4. Conclusion

The effects of adding various BBC glass concentration and 1.0 wt.% excess PbO on the sintering and piezoelectric properties of 12PNS–40PZ–48PT ceramics have been studied. The results in the present investigation are summarized as follows:

1. When BBC glass (2.0–5.0 wt.%) is added to the 12PNS–40PZ–48PT ceramics and sintered at 925°C for 2 h, the powders coexist with both tetragonal and rhombohedral phases.
2. For the composition of 12PNS–40PZ–48PT added with 2.0 to 5.0 wt.% BBC glass and sintered at 950°C for 2 h, the principal crystalline phase has a perovskite structure, and pyrochlore is also appeared.
3. With the specimen containing 1.0 wt.% BBC glass, the bulk density increases from 7.36 to 7.54 g·cm^{-3} with sintering temperature increasing from 900 to 975°C. When the compact contains 2.0 wt.% BBC glass and sintered at 975°C for 2 h, the maximum bulk density, 7.86 g·cm^{-3}, is obtained. But for BBC glass concentration greater than 2.0 wt.%, the bulk density decreases with increasing BBC glass concentration.
4. The sintering temperature of the 12PNS–40PZ–48PT ceramics is reduced to lower than 1000°C by adding BBC glass and a density of 97.5% of the theoretical is obtained after sintered at 925°C for 2 h.
5. When the compact contains 1.0–5.0 wt.% BBC glass and sintered at 975°C for 2 h, the K_p value decreases from 0.48 to 0.30. For the compact sintered at 950°C for 2 h, the K_p value increases from 0.48 to 0.51 for the BBC glass concentration between 1.0 and 2.0 wt.%. On the other hand, the K_p value decreases from 0.51 to 0.30 as the addition of BBC glass increases from 2.0 to 5.0 wt.%.
6. The Q_m value increases with the BBC glass content increasing from 2.0 to 4.0 wt.% when sintered at 925°C for 2 h.

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