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Low-temperature sintering of $12Pb(Ni_{1/3}Sb_{2/3})O_3$–$40PbZrO_3$–$48PbTiO_3$ with V_2O_5 and excess PbO additives

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Abstract

Low-temperature sintering of $12Pb(Ni_{1/3}Sb_{2/3})O_3$–$40PbZrO_3$–$48PbTiO_3$ (12PNS–40PZ–48PT) calcined powders with V_2O_5 and excess PbO additives has been investigated. Adding 0.20 to 0.40 wt.% V_2O_5 and 1.0 wt.% excess PbO to 12PNS–40PZ–48PT calcined powders and sintering at 950 °C for 4 h, the sintered samples only contain the perovskite structure. The calcined powders are doped with 3.0 wt.% excess PbO and 0.20 to 1.0 wt.% V_2O_5 and sintered at 950 °C for 4 h, the coexistence of both tetragonal and rhombohedral phases with the minor phase of pyrochlore is observed. During the calcined powders contain 1.0 wt.% excess PbO and are sintered at 950 to 975 °C for 2 h, the bulk density decreases with V_2O_5 addition greater than 0.6 wt.%. When the calcined powders with 3.0 wt.% excess PbO are sintered at 900 to 975 °C for 2 h, the bulk density decreases with added V_2O_5 content increased. The values of the planar coupling coefficient (K_p) approach the maxima, namely, 0.51 obtained for the compacts containing 0.40 wt.% V_2O_5 and 1.0 wt.% excess PbO and sintered at 950 °C. As the calcined powders are added with 3.0 wt.% excess PbO and 0.80 wt.% V_2O_5 and sintered at 975 °C for 2 h, the maximum Q_m value 1100 is obtained. © 2002 Elsevier Science Ltd. All rights reserved.

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

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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 compositions and microstructure 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 detail the physics of piezoelectric ceramics.[2] Shirane et al.[3,4] have studied lead zirconate–lead titanate solid solution and found a morphotropic phase transformation. The crystal structure changes from tetragonal to rhombohedral in the vicinity of Zr/Ti = 53/47 corresponding to a composition of the morphotropic phase boundary.[5] Jaffe et al.[6] have also found excellent piezoelectric properties as well in the composition $Pb(Zr_{0.55}Ti_{0.45})O_3$ near the morphotropic phase boundary.

The PZT ceramics have been prepared by a mixed oxide technique. In the conventional sintering of PZT-type ceramics, control of the atmosphere and sintering temperature is critical due to the evaporation of PbO.[7] Typically, packing powders and/or pellets containing excess PbO and $PbZrO_3$ or PbO–$PbZrO_3$ mixtures are used to provide a positive PbO vapor pressure surrounding the PZT ceramics during sintering.[8–10] On the other hand, several workers have attempted to control or eliminate the loss of PbO by using hot pressing followed by heat treating in a PbO atmosphere,[10] addition of excess PbO during the material batching,[11,12] hot-pressing in oxygen,[13,14] use of multiphase crucibles,[15] and improved powder preparation.[16–18]

The development of low-sintering temperature piezoelectric ceramics could reduce energy consumption and environmental pollution and enable the ceramics to be cofired with less expensive metals in multilayer devices.[19] Gui et al.[19] have reported that the sintering temperature of PZT ceramics can be reduced from near 1250 to about 960 °C by the addition of a small amount of the lower melting frit, B_2O_3–Bi_2O_3–CdO. Wang et al.[20] have reported the effect of various amounts of $30B_2O_3$–$25Bi_2O_3$–45CdO (BBC) glass powders and 1.0 wt.% excess

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PbO on the $12Pb(Ni_{1/3}Sb_{2/3})O_3$–$40PbZrO_3$–$48PbTiO_3$ (12PNS–40PZ–48PT) ceramics, 97.5% of the theoretical density is obtained for the compact containing 2.0 wt.% BBC glass and 1.0 wt.% excess PbO after sintered at 925 °C for 4 h. Wittmer and Buchanan[21] have pointed out that the addition of 0.10 to 6.0 wt.% V_2O_5 to PZT ceramics promotes rapid densification below 975 °C, thereby eliminating the need for PbO atmosphere control .

In our previous study, the base composition of $Pb(Ni_{1/3}Sb_{2/3})O_3$ (PNS) = 12 mol%, $PbZrO_3$ (PZ) = 40 mol% and $PbTiO_3$ (PT) = 48 mol% was the morphotropic phase boundary (MPB) in the xPNS−(52−x) PZ−48PT ($4 \leqslant x \leqslant 14$) and 12PNS-(88−$y$)PZ−$y$PT($44 \leqslant x \leqslant 52$) piezoelectric ceramics systems.[22] Hence the present work was undertaken to investigate the effect of V_2O_5 and excess PbO addition on the low-temperature sintering of the 12PNS–40PZ–48PT ceramics. The object of this study is to reduce the sintering temperature of the 12PNS–40PZ–48PT ceramics, while maintaining desirable piezoelectric properties. In this paper, the following four aspects were studied as follows: (i) to present the phase stability and compare that with the addition of V_2O_5 and excess PbO and sintering temperature at the same time; (ii) to evaluate the relationship between among bulk density, V_2O_5 additive content and sintering temperature; (iii) assess the effect of various additive contents on the microstructure of the 12PNS–40PZ–48PT ceramics during sintering; and (iv) to evaluate the relationship between planar coupling coefficient (K_p) and mechanical quality coefficient (Q_m) and the V_2O_5 additive content and sintering temperature.

2. Experimental procedure

2.1. Sample preparation

The base composition of this study was $Pb(Ni_{1/3}Sb_{2/3})O_3$ = 12 mol%, $PbZrO_3$ = 40 mol%, $PbTiO_3$ = 48% (12PNS–40PZ–48PT), 1.0 and 3.0 wt.% excess PbO were added to the base composition, respectively. Additive amounts of V_2O_5 were added to the host 12PNS–40PZ–48PT ceramic powders in concentration varying from 0.20 to 1.0 wt.%.

The 12PNS–40PZ–48PT ceramic powders with excess PbO were prepared by the mixed-oxide technique. V_2O_5 was added after the calcination at 850 °C for 2 h. The flow chart of the preparation of the 12PNS–40PZ–48PT calcined powders with V_2O_5 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 FERAK, 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-homogenized with distilled water for 8 h using high purity Al_2O_3 balls (SSA-S standard, 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 2 h with a heating and cooling rate of 350 °C·h^{-1}. The calcined powders were reground using wet ball-milling for 15 min, then dried and sifted.

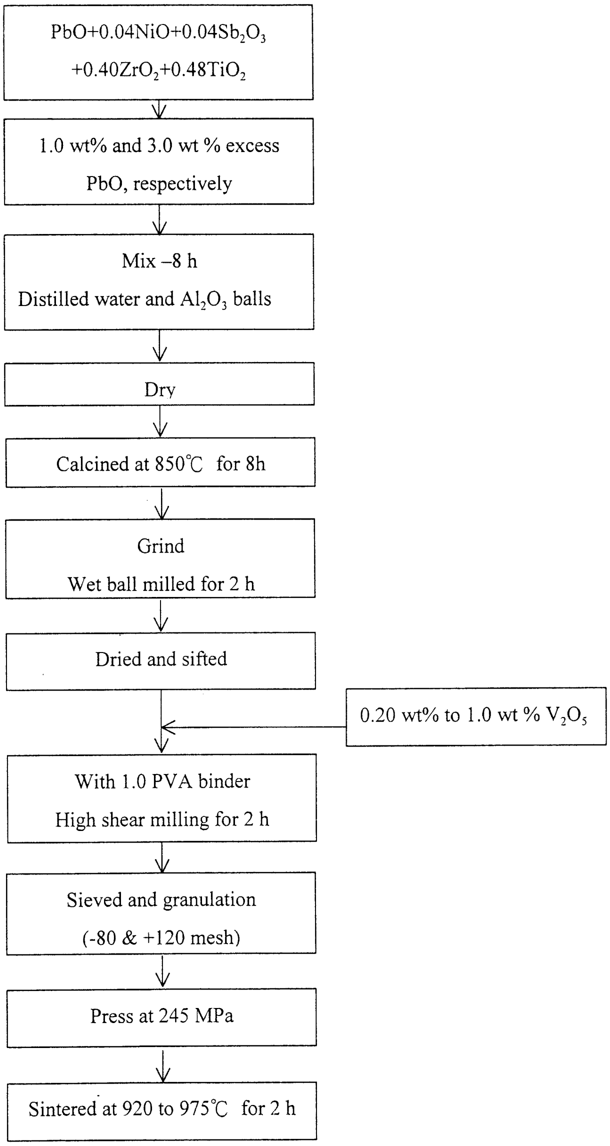

Fig. 1. Flow chart for the preparation of the 12PNS–40PZ–48PT calcined powders with excess PbO and V_2O_5.

The fine calcined powders were mechanically blended with 0.20 to 1.0 wt.% V_2O_5 powders (purity > 99%, supplied by Merck, Germany) and a 1.0 wt.% PVA binder in a high-shear milling for 2 h and sieved after granulation. After granulation the powder mixture was isostatically pressed at 245 MPa into a pellets of 1.50 mm in height and 12.0 mm in diameter.

Finally, the pellets were sintered in a sealed alumina crucible between 900 and 975 °C for 2 h at a heating rate of 4 $^\circ C \cdot min^{-1}$.[23] The sintered compact was lapped to a thickness of 1.00 mm. Electrodes were made by painting with silver paste and firing at 780 °C for 20 min.

2.2. *Analysis*

After sintering, the bulk densities of sintered samples was measured by using an Archimedes method and calculated by Eq. (1)

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

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

The crystalline phase was identified by X-ray diffration (XRD) analysis. The XRD work was performed with a Ragaku X-ray diffractometer (model rad ΠA, Rigaku, Tokyo) with CuK_α radiation and a Ni filter, at a scanning rate (2θ) of $0.25^\circ \cdot min^{-1}$.

The fracture surface of the sintered specimens was examined by scanning electron microscopy (SEM, Jeol 840, Tokyo).

Preceding the piezoelectric properties measurements, the sintered specimens were poled in a silicone oil at 100 °C by applying a static field of 3.5 $kV \cdot min^{-1}$ for 1 h. The specimens were field-cooled to room temperature in 30 min. Twenty-four hours after poling, the planar coupling coefficient (K_p)[24] and mechanical quality coefficient (Q_m)[25] were calculated by Eqs. (2) and (3), respectively,

$$K_p = \left[2.51(fa - fr)^2 \cdot fr^{-1}\right]^{1/2} \tag{2}$$

and

$$Q_m = fa^2\left[2\pi RrCfr\left(fa^2 - fr^2\right)\right]^{-1} \tag{3}$$

where	fa	antiresonant frequency (Hz),
	fr	resonant frequency (Hz),
	Rr	resonant resistance (ohms),
	C	capacitance (farads).

3. Results and discussion

3.1. *Effect of V_2O_5 and PbO addition on the phases stability*

In the present study, the base composition of PNS = 12 mol%, PZ = 40 mol% and PT = 40 mol% was at the morphotropic phase boundary (MPB) in the xPNS–$(52-x)$PZ–48PT ($4 \leqslant x \leqslant 14$) and 12PNS–$(88-y)$ PZ–yPT ($44 \leqslant y \leqslant 52$) piezoelectric ceramic systems.[22] The chemical compositions for the tetragonal side of MPB are well known for optimized electrical properties.

The typical X-ray diffraction (XRD) patterns of the 1.0 wt.% excess PbO-doped 12PNS–40PZ–48PT piezoelectric powders added with various V_2O_5 contents and sintered at 950 °C for 4 h are shown in Fig. 2. It indicates that these sintered ceramics added with 0.20 and 0.40 wt.% V_2O_5 only contain the perovskite structure. But as the V_2O_5 content increased from 0.60 to 1.0 wt.%, the piezoelectric perovskite structure is often associated with an parasitic phase of pyrochlore. The formation of the pyrochlore phase is due to the excese phase in composition containing beyond 0.60 wt.% V_2O_5.

The typical XRD patterns of the 3.0 wt.% excess PbO-doped 12PNS–40PZ–48PT piezoelectric powders added with various amounts of V_2O_5 and sintered at 950 °C for 4 h are shown in Fig. 3. It indicates that the addition of V_2O_5 content from 0.20 to 1.0 wt.% shows in all cases the coexistence of both tetragonal (F_T) and rhombohedral (F_R) phases as revealed by the splitting of the (2 0 0) peak reflection into $(2\ 0\ 0)_R$ and $(0\ 0\ 2)_T$ peaks. The reflection indexed with T is assigned to the tetragonal piezoelectric phase, F_T, whereas that indexed with R to the rhombohedral phase, F_R. The coexistence of both piezoelectric phases at the MPB composition has been previousely demonstrated by XRD in different piezoelectric ceramic systems by splitting of the (2 0 0) diffraction peak only,[26,27] the two peaks (2 0 0) and (2 2 2),[28] (2 0 0) and (2 1 1), [22] the three peaks (1 0 0), (2 0 0) and (1 1 2), [21] or

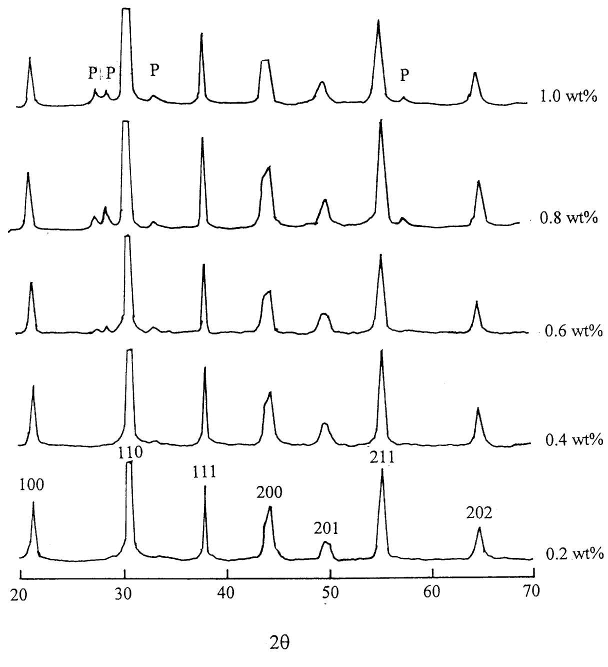

Fig. 2. XRD patterns of the 12PNS–40PZ–48PT calcined powders containing 1.0 wt.% excess PbO and various V_2O_5 contents and sintered at 950 °C for 4 h. P, pyrochlore.

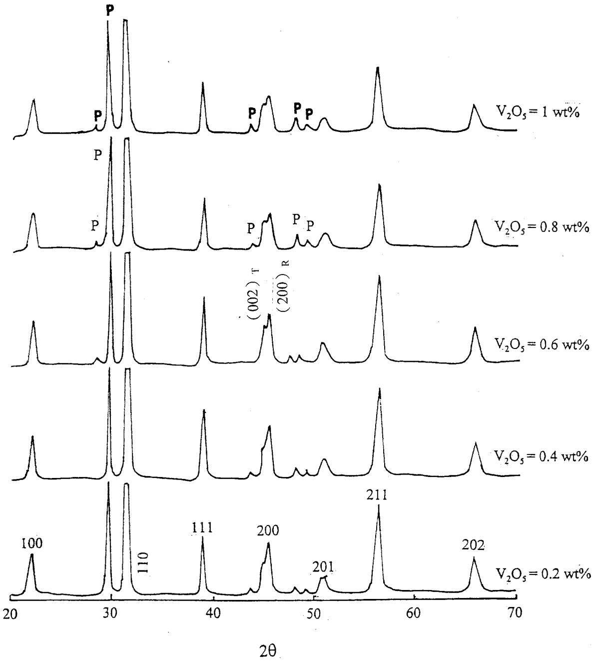

Fig. 3. XRD patterns of the 12PNS–40PZ–48PT calcined powders containing 3.0 wt.% excess PbO and various V_2O_5 contents and sintered at 950 °C for 4 h. P, pyrochlore.

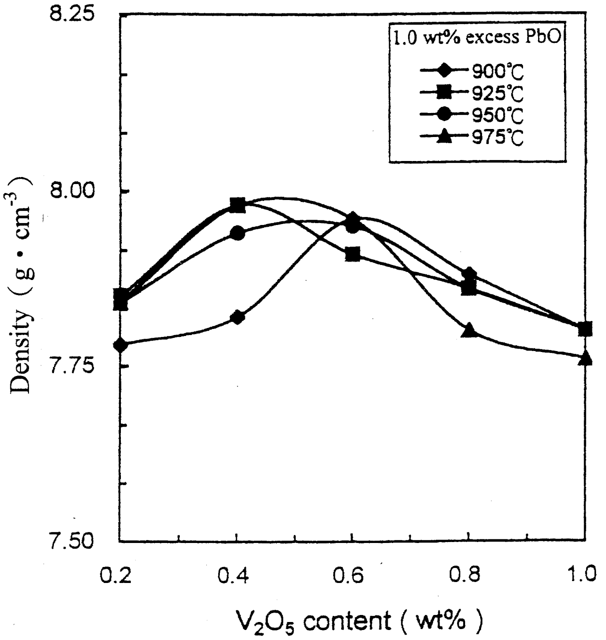

Fig. 4. Relationship among bulk density, V_2O_5 content and sintering temperature of the base composition 12PNS–40PZ–48PT calcined powders containing 1.0 wt.% excess PbO.

splitting of the (h 0 0)- and (h 0 1) peaks in the triplets of the $(0\ 0\ h)_T$, $(h\ 0\ 0)_R$, and $(h\ 0\ 0)_T$, $(h\ 0\ 1)_T$, $(h\ 0\ 1)_R$ and $(1\ 0\ h)_T$ peaks, respectively.[7]

From Fig. 3, it is also found that even only with 0.20 wt.% V_2O_5 addition to the 12PNS–40PZ–48PT containing 3.0 wt.% excess PbO and sintered at 950 °C for 4 h the minor crystalline phase of pyrochlore is also present. This result is caused by the excess PbO and V_2O_5 at 350 °C, which are present as a liquid phase[21] and easily react with the 12PNS–40PZ–48PT piezoelectric powders to form the pyochlore phase during sintering. Hence, the low-temperature sintering of the 12PNS–40PZ–48PT with 3.0 wt.% excess PbO do not need much excess PbO to prevent or control the lead loss and produce a material with enhanced or more consistent properties.

Figs. 2 and 3 indicates that when the specimens of the same composition are sintered at 950 °C for 4 h, the XRD reflection intensity of the pyrochlore phase of the 12PNS–40PZ–48PT with 3.0 wt.% excess PbO is greater than with 1.0 wt.% excess PbO for the same amount of added V_2O_5. Hence, the crystalline phases obtained from these sintered specimens are clearly composed of the mixed phases of each solid solution without any change in the mixing ratio of each phase over the temperature range.

3.2. Bulk density of the sintered specimens

The bulk density for the base composition of the 12PNS–40PZ–48PT calcined powders added with 1.0 wt.% excess PbO and sintered at various temperatures for 2 h is a function of V_2O_5 content as shown in Fig. 4. It indicates that, with the specimens containing V_2O_5 from 0.20 to 0.40 wt.% the bulk density 7.91 g·cm^{-3} [98.9% theoretical, based on the XRD value of 8.0 g·cm^{-3} for an unmodified PZT (53–47)] is obtained for the samples containing V_2O_5 0.40 wt.% and sintered at 925 and 975 °C for 2 h, respectively. During the addition of only 0.20 wt.% V_2O_5, insufficient liquid amount leads to poor wetting of the grain boundaries. In the liquid phase sintering the formation of a poor wetting liquid may lead to swelling of the compact during heating without densification,[29] resulting in bulk density less than 7.91 g·cm^{-3}. On the other hand, the bulk density decreases with V_2O_5 addition greater than 0.60 wt.% and this result is attributed to the formation of a lower-density second phase.

For the compact containing 3.0 wt.% excess PbO, the effect of sintering temperature and V_2O_5 content on the bulk density is shown in Fig. 5. It indicates that when the samples is sintered at 900 °C for 2 h, within experimental error the bulk density decreases from 7.96 to 7.75 g·cm^{-3} (96.9% theoretical) with added V_2O_5 increases from 0.20 to 1.0 wt.%. The trends of the bulk density variation for samples sintered at 900–950 °C are same sintered at 975 °C, i.e. the bulk density decreases with added V_2O_5 increased. According to Figs. 2–4, this result can be caused the parasitic phase of pyrochlore formation. On the other hand, Wittmer and Buchanan[21] also have reported that the sintered density decreases with increasing V_2O_5 addition for the samples sintered in air at 940–975 °C for 2 h. In the present study,

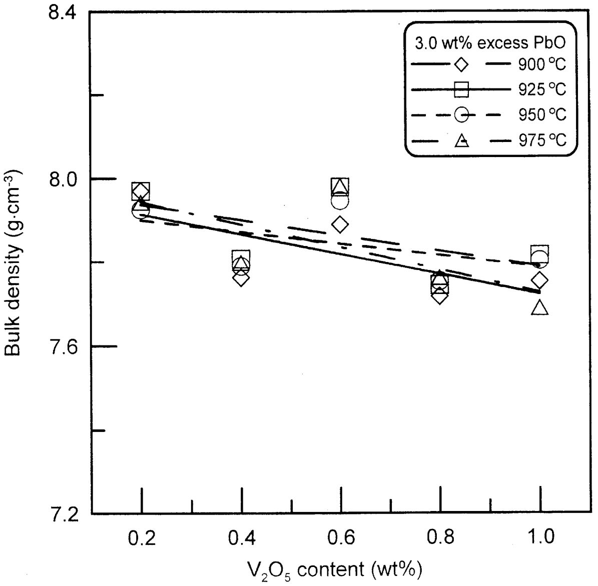

Fig. 5. Relationship among bulk density, V_2O_5 content and sintering temperature of the base composition 12PNS–40PZ–48PT calcined powders containing 3.0 wt.% excess PbO.

instead of PbO atmosphere control, the addition 3.0 wt.% excess PbO and various V_2O_5 additive are used. The V_2O_5 additive is easily absorbed on the PZT particle surface and forms a complex lead vandate at $\geqslant 350$ °C.[21] This phenomenon reduces the liquid phase sintering and the initial density decreases with increasing V_2O_5 content.

3.3. Microstructures of the sintered samples

The SEM micrographs of the fracture surface of the compacts containing differents V_2O_5 and various excess PbO and sintered at various temperatures for 2 h are shown in Fig. 6. The SEM micrographs shows the presence of a number of large pores. Besides, it also indicates the grains of the samples sintered at 900 °C for 2 h [Fig. 6(a)] maintain their initial morphology. When sintering at 900 °C the average grain size from 0.60 to 1.8 μm is practically the same, but sintered at 975 °C [Fig. 6(b)] this value (3.0 μm) is greater than at 900 °C. On the other hand, when sintering at 975 °C, the grains have the different morphology. The different sizes as well as the morphological modification of the grains are noticeable in these samples. Fig. 6(c) shows the sample containing 1.0 wt.% excess PbO and added V_2O_5 0.40 wt.% and sintered at 950 °C for 2 h. It seens that the grain size become more uniform due to material transfer from a liquid phase, but the wider boundary still exist. The SEM micrograph of sample added V_2O_5 0.80 wt.% and 1.0 wt.% excess PbO and sintered at 950 °C for 2 h is shown in Fig. 6(d). It found that most of the grains precipitated from the liquid phase have sharp corners and thinner boundaries. Fig. 6(e) shows the SEM micrograph of the sample added V_2O_5 0.80 and 3.0 wt.% excess PbO and sintered at 950 °C for 2 h. It seen that a very small amount of the liquid phase remains in the grain boundaries and reabsorbed in the grains, but yet contains a large pore fraction.. A liquid phase that promotes densification of the material appears in the initial and intermediate stages of sintering, then the liquid phase is reabsorbed in the grain in the final stage of sintering.[19] Wittmer and Buchauan[21] have pointed out two factors contributing to the development of a more uniform microstructure of mill-addition samples: (i) the larger initial particle size is due to the higher calcination temperature of the PZT powders prior to the mill-addition of V_2O_5; and (ii) the probable presence of a liquid phase.

3.4. K_p and Q_m value of the sintered samples

The relation between K_p value and V_2O_5 content of the 12PNS–40PZ–48PT calcined powders added with 1.0 wt.% excess PbO and sintered at various temperatures for 2 h is shown in Fig. 7. It indicates that, the sintered sample has the highest value, 0.51 when the compact contains 0.40 wt.% V_2O_5 and is sintered at 950 °C. The K_p value increases with the V_2O_5 content varying from 0.20 to 0.40 wt.% and sintered at 900–975 °C. However, the K_p value decreases with the V_2O_5 content varying from 0.60 to 1.0 wt.%. Although Bystrikov[30] has pointed out that during the formation of PZT, the diffusion of V^{4+} into the PZT lattice depletes the vanadium content of the boundary phase. Similarly, Wittmer and Buchauan[21] have also reported that the V^{4+} content is found to induce lattice distortion while it is increased by the presence of V_2O_5 during the formation of the PZT. However, as shown in Fig. 2, these results can be caused by the volatilization of PbO whicle generally leads to the formation and growth of the pyrochlore phase.

Fig. 8 shows the relationship between K_p value and V_2O_5 content of the 12PNS–40PZ–48PT calined powders containing 3.0 wt.% excess PbO and sintered between 900 and 975 °C for 2 h. It shows that the K_p value decreases as the V_2O_5 content increases from 0.20 to 1.0 wt.%. From Figs. 3, 7 and 8, it is evident that for the same amount of V_2O_5 additive, increasing the excess PbO content leads to the formation of the pyrochlore phase which results in a degradation of K_p value.

The relationship between Q_m value and V_2O_5 content of the 12PNS–40PZ–48PT calcined powders containing 1.0 wt.% excess PbO and sintered between 900 and 975 °C for 2 h is shown in Fig. 9. It indicates that, as the V_2O_5 content increases from 0.20 to 0.40 wt.%, the Q_m value gradually increases from 122 to 131, and 133 to 138, for the samples sintered at 900 and 925 °C, respectively. Conversely, the Q_m value decreases from 131 to 122, and 167 to 119, for the samples sintered at 950 and 975 °C, respectively. When added V_2O_5 increases from

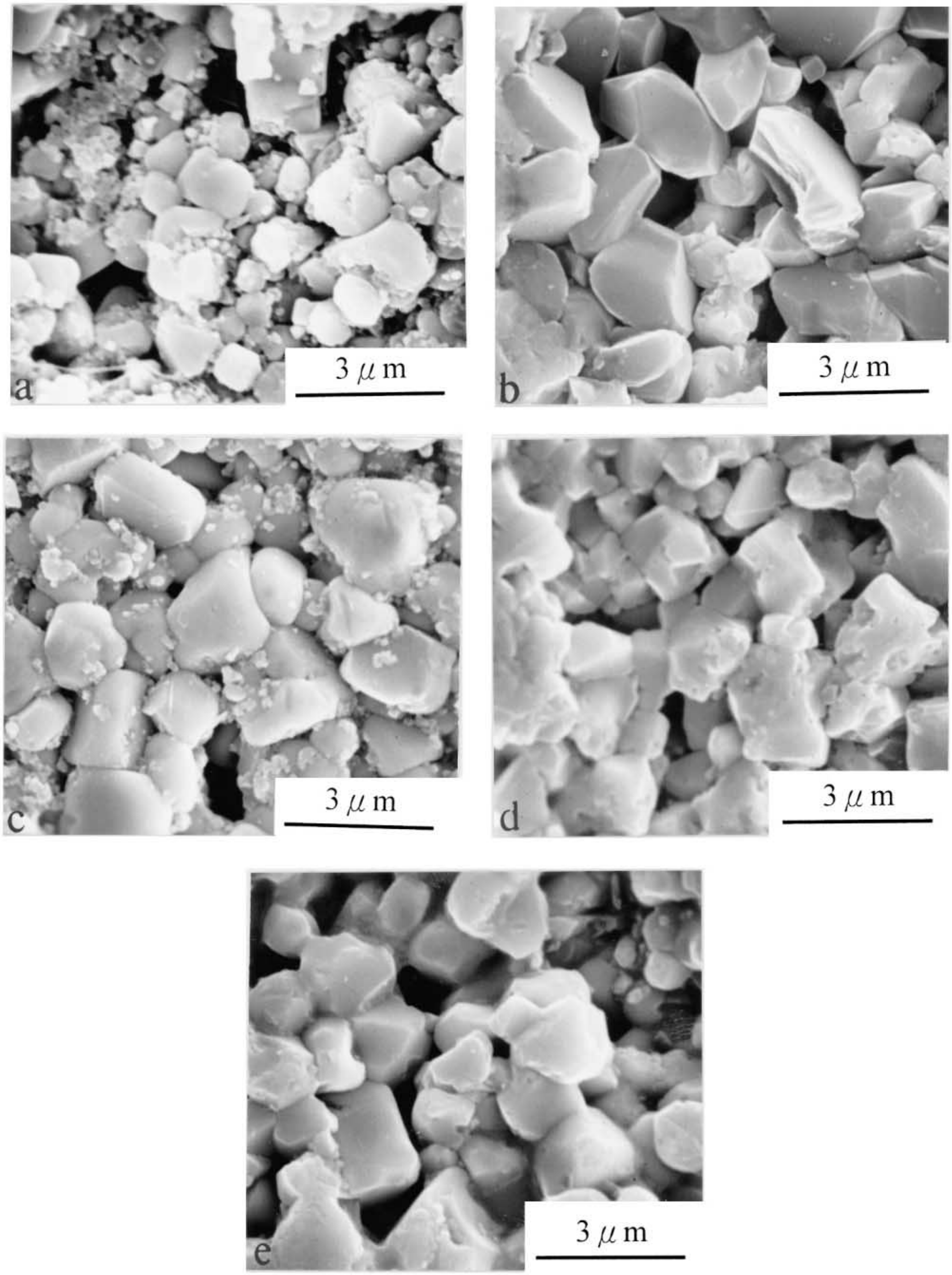

Fig. 6. SEM micrographs of the 12PNS–40PZ–48PT calcined powder added various V_2O_5 and excess PbO and sintered at various temperatures for 2 h: (a) V_2O_5 0.40 wt.% and excess PbO 1.0 wt.%, sintered at 900 °C, (b) V_2O_5 0.40 wt.% and excess PbO 1.0 wt.%, sintered at 975 °C, (c) V_2O_5 0.40 wt.% and excess PbO 1.0 wt.%, sintered at 950 °C, (d) V_2O_5 0.80 wt.% and excess PbO 1.0 wt.%, sintered at 950 °C, and (e) V_2O_5 1.0 wt.% and excess PbO 3.0 wt.%, sintered at 950 °C.

0.4 to 1.0 wt.%, the Q_m value increases from 119–213 for the samples sintered at 975 °C. On the other hand, the trends of the Q_m variation for the samples sintered at 900–950 °C are same as that sintered at 975 °C. The maximum Q_m attains to 218 for the calcined powders containing 1.0 wt.% excess PbO and 1.0 wt.% V_2O_5 and sintered at 925 °C for 2 h.

Fig. 10 shows the relationship between Q_m value and V_2O_5 content of the 12PNS–40PZ–48PT powders added with 3.0 wt.% excess PbO and sintered at 900 to 975 °C for 2 h. It indicates that, the Q_m value increases from 250–304 for the samples containing V_2O_5 from 0.20 to 0.60 wt.% and sintered at 975 °C. This value is higher than the result of Fig. 9. The Q_m value (1100) shows a sudden increase for the compact containing 0.80 wt.% V_2O_5. This result can expect that the internal bias field prohibits the domain wall mortion under a small electric signal which is used for the Q_m-measurement even at room temperature. This is probably the cause of the high Q_m value.[31] When the V_2O_5 content is higher than 0.80 wt.%, the Q_m value decreases due to the increasing amount of the pyrochlore phase for sintering at 900 to 975 °C.

In our previous studies of the xPNS–(52−x)PZ−48PT ($4 \leqslant x \leqslant 14$) and 12PNS–(88−$y$)PZ–$y$PT ($44 \leqslant y \leqslant 52$) piezoelectric ceramic systems, the morphotropic phase boundary has been found in these systems.[22] The object of adding excess 0.5–7.0 wt.% PbO to the 12PNS–40PZ–48PT, piezoelectric ceramic system with no additives and sintering at 1280 °C for various times is to eliminate the need for a controlled PbO atmosphere.[32] The object of adding $30B_2O_3$–$25Bi_2O_3$–45CdO (mol%) glass with 1.0 wt.% excess PbO on the sintering 12PNS–40PZ–48PT piezoelectric ceramics is to reduce the sintering temperature of the 12PNS–40PZ–48PT ceramics and eliminate the need for a controlled PbO atmosphere, while maintaining describle piezoelectric properties.[20]

In the present study, for the 12PNS–40PZ–48PT calcined powders containing 3.0 wt.% excess PbO and 0.80

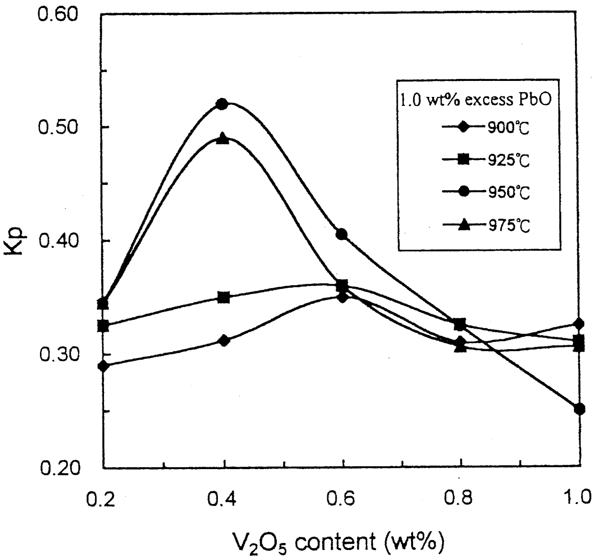

Fig. 7. Relationship between K_p value and V_2O_5 content in the 12PNS–40PZ–48PT calcined powders added with excess PbO 1.0 wt.% and sintered at various temperatures for 2 h.

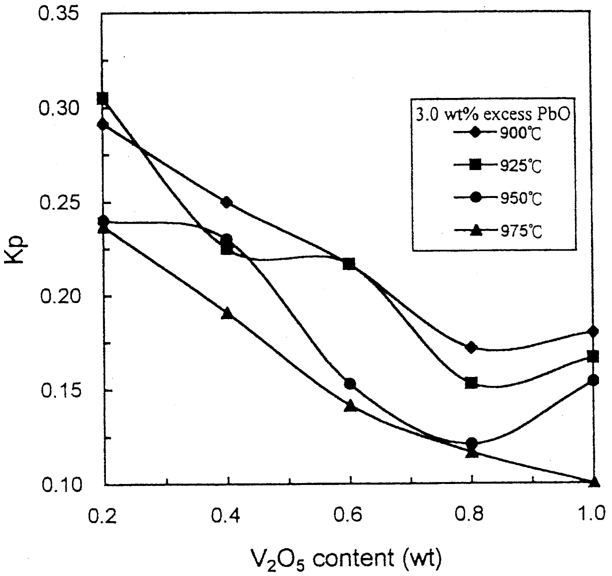

Fig. 8. Relationship between K_p value and V_2O_5 content in the 12PNS–40PZ–48PT calcined powders containing 3.0 wt.% excess PbO and sintered at various temperatures for 2 h.

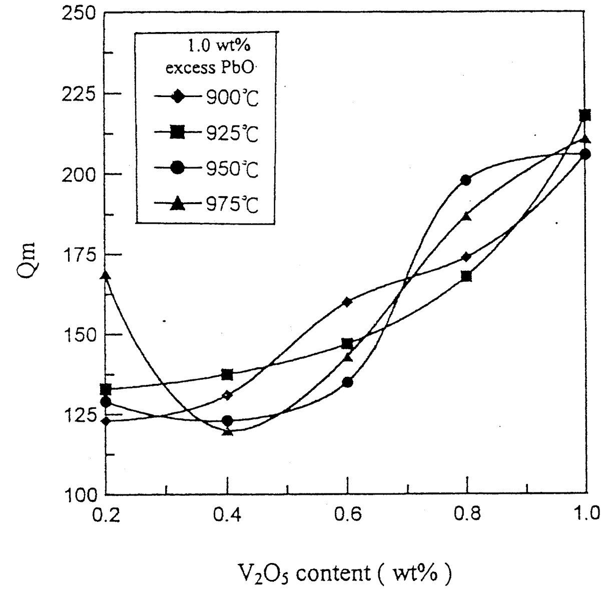

Fig. 9. Relationship between Q_m valve and V_2O_5 content in the 12PNS–40PZ–48PT calcined powders containing 1.0 wt.% excess PbO and sintered at various temperatures for 2 h.

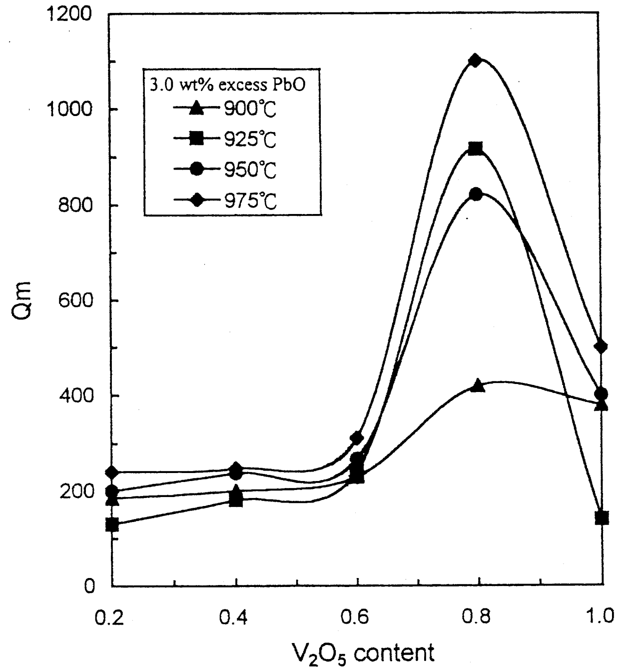

Fig. 10. Relationship between Q_m value and V_2O_5 content in the 12PNS–40PZ–48PT calcined powders containing 3.0 wt.% excess PbO and sintered at various temperatures for 2 h.

wt.% V_2O_5 and sintered at 975 °C for 2 h the maximum Q_m value 1100 was obtained. This value is higher than the base composition (i.e. 12PNS–40PZ–48PT) sintered at 1280 °C for 2 h ($Q_m = 300$).[22] For the 12PNS–40PZ–48PT powders added with 3.0 wt.% excess PbO and sintered at 1280 °C for 2 h, $Q_m = 314$ is obtained[32] and for the 12PNS–40PZ–48PT powders added with 4.0 wt.% $30B_2O_3$–$25Bi_2O_3$–45CdO glass and sintered at 900 °C for 2 h, $Q_m = 460$ is obtained.[20]

4. Conclusions

The effects of V_2O_5 and excess PbO addition on the low-temperature sintering of 12PNS–40PZ–48PT calcined powders have been studied. The results in the present study are summerized as follows:

(1) When 1.0 wt.% excess PbO-doped 12PNS–40PZ–48PT calcined powders are added with 0.20 to 0.40 wt.% V_2O_5 and sintered at 950 °C for 2 h, the sintered sample only contains the perovskite structure. As the V_2O_5 content increases from 0.60 to 1.0 wt.%, the perovskite structure is often associated with the pyrochlore phase.

(2) When 3.0 wt.% excess PbO-doped 12PNS–40PZ–48PT calcined powders are added with 0.20 to 1.0 wt.% V_2O_5 and sintered at 950 °C for 2 h, the XRD patterns show in all cases the coexistence of both tetragonal and rhombohedral phases as the major phases and the minor phase of pyrochlore is also observed as well.

(3) When the 12PNS–40PZ–48PT calcined powders containing 0.20 to 0.40 wt.% V_2O_5 are added with 1.0 wt.% excess PbO and sintered at 925 to 975 °C for 2 h, the bulk density 7.91g·cm^{-3} (98.9% of theoretical) is obtained. Conversely, the bulk density decreases when V_2O_5 content is greater than 0.60 wt.%.

(4) For the compact containing 3.0 wt.% excess PbO and various V_2O_5 contents, when sintered at 975 °C for 2 h, the bulk density decreases from 7.96 to 7.75 g·cm^{-3}, as the V_2O_5 content increases from 0.20 to 1.0 wt.%. The trends of bulk density variation for the samples sintered at 900 to 950 °C are the same as that sintered at 975 °C, namely, the bulk density decreases with added V_2O_5.

(5) As the 12PNS–40PT–48PZ calcined powders are added with 1.0 wt.% excess PbO and various V_2O_5 contents, the K_p value increases with the V_2O_5 content varying from 0.20 to 0.40 wt.%, all compacts being sintered at 900 to 975 °C for 2 h. Conversely, the K_p value decreases with the V_2O_5 content increasing from 0.60 to 1.0 wt.%.

(6) When 3.0 wt.% excess PbO doped 12PNS–40PZ–48PT calcined powders are added with various V_2O_5 contents and sintered at 900 to 975 °C for 2 h, the K_p value decreases with the V_2O_5 content increasing from 0.2 to 1.0 wt.%.

(7) When 1.0 wt.% excess PbO-doped 12PNS–40PZ–48PT calcined powders are added with 0.20 to 0.40 wt. V_2O_5 and sintered between 900 and 925C, the Q_m value gradually increases with V_2O_5 content. Conversely, the Q_m value decreases when the compact is sintered at 950 to 975 °C. On the other hand, the Q_m value increases with the V_2O_5 content increasing from 0.40 to 1.0 wt.% when the compacts are sintered at 925 to 975 °C for 2 h.

(8) As the 12PNS–40PZ–48PT calcined powders containing 3.0 wt.% excess PbO are added with V_2O_5 from 0.20 to 0.60 wt. , the Q_m value increased from 250 to 304 for the samples sintered at 900 to 975 °C for 2 h. When the sample containing 0.80 wt.% V_2O_5 and sintered at 975 °C for 2 h, the maximum Q_m value, 1100 is obtained.

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