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$Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics sintered with Li_2CO_3 and Na_2CO_3: improvement of characteristics

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The electrical characteristics of PZT 52/48 and PZTN 52/48 could be improved with a pair doping method, i.e. by doping monovalent cation R^+ with an equal amount of trivalent cation R^{3+}. The doping pairs could promote the densification of the ceramics and provide charge compensation for the unbalanced charge arising from Li_2CO_2 or Na_2CO_3 doping. The pair doping method also released the problem of adding excess PbO for compensation of PbO evaporation in sintering and as liquid-phase former. Since the doping pair, such as the Li–Bi pair, could serve as a liquid-phase former, also, but with improved characteristics. If the samples were sintered under appropriate conditions, the obtained characteristics were comparatively process-insensitive. The optimal sintering conditions were at 1050° C for 2 h. With the Li–Bi doping pair and sintered under these conditions, the PZTN 52/48 could have a k_p of about 60%, frequency constant N of about 1840 kHz mm, Q_m of about 255 and ε^T_{33} of about 1070.

1. Introduction

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (abbreviated as PZT 52/48) piezoelectric ceramics have a composition near the morphotropic phase boundary of $PbTiO_3$–$PbZrO_3$ system, [1] and has been used extensively in piezoelectric field because of its high activity [2]. Many researches have been done to arrive at either a low temperature sinterable process [3] or better electrical characteristics [4] of this composition. In this study, both objectives were encountered by taking both liquid-phase sintering and charge compensation of crystal lattice into consideration, simultaneously.

The lowering of sintering temperature of PZT 52/48 when sintered with Li_2CO_3 and Na_2CO_3 had been discussed previously [5]. However, the electrical properties of the sintered ceramics in these causes were comparatively process-sensitive [6]. Which was attributed to both the decomposition of carbonates and the diffusion of small cations Li^+ and Na^+ into the lattice of PZT52/48. In order to overcome this shortcoming, donor–acceptor pair doping was applied by incorporating trivalent cations, such as Bi^{3+} or La^{3+}, into the Li^+- or Na^+-doped PZT 52/48. This pair doping would provide both the charge compensation between the doped cations, as stated by Jyumonji *et al.* [7] and the liquid-phase sintering.

One of the most useful piezoelectric ceramics is niobium-modified Pb(Zr, Ti)O_3 ceramics [8]. So the pair doping method had also been applied to the composition of $Pb[(Zr_{0.52}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$ (abbreviated as PZTN 52/48), and compared with the results of the pair-doped PZT 52/48. Both PbO-rich and PbO-deficient cases were to be studied in the pair-doped PZTN 52/48.

2. Experimental procedure

Raw materials of PbO, TiO_2, ZrO_2 and Nb_2O_5 were weighed in appropriate proportionalities separately, followed by wet-mixing in a ball miller and then drying. The dried mixtures were calcined at 925° C and then pulverized and mixed with suitable amount of dopants which consist of trivalent cations in oxides form and monovalent cations in carbonates form together. The mixtures were pressed into disc-type samples under 400 kg cm^{-2} pressure. Sintering of these samples was conducted at temperatures from 900 to 1150° C for 2 h.

In order to prevent PbO from evaporation, an equilibrium PbO vapour pressure was established by using Pb(Zr, Ti)O_3 as setter and put the samples into a 100 cm SSA-S grade Al_2O_3 crucible covered with a tight lid. It seemed more appropriate that comparisons of the properties were confined to the chosen compositions only, since the sintering atmospheres were almost equivalent in those cases.

After sintering, the samples were subjected to annealing at 930° C to provide more evidence in confirming the effects of doping. The temperature 930° C was chosen because the second phase, which arose from the additives and segregated at the grain boundary, and part of the interstitial cations could be driven out at this temperature if annealing time was sufficient. After the electrodes were printed and fired on the samples, the dielectric properties of those sintered samples were measured with a HP 4270A capacitance bridge. X-ray diffraction analysis had been done, on the ground powders of the sintered samples, to study the variations of the lattice constants. The lattice constants were obtained from the average values of the X-ray diffraction results in the (1 1 0) and (2 1 1) directions.

Before measuring the piezoelectric properties of the sintered samples, the samples were polarized under 2.5 kV mm^{-1} field at 90° C for 30 min, and then

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TABLE I Basic composition together with the kind and amount of the additives for group A to group G.

Group	Basic composition	Additives
A	$Pb(Zr_{0.52}Ti_{0.48})O_3$	0.375 wt % Li–Bi
B	$Pb[(Zr_{0.52}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$	9 wt % PbO
C	$Pb[(Zr_{0.52}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$	3 wt % PbO 0.375 wt % Li–Bi
D	$Pb[(Zr_{0.52}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$	0.375 wt % Li–Bi 0.025 wt % Li_2CO_3
E	$Pb[(Zr_{0.52}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$	0.375 wt % Li–La
F	the same as group D but annealing at 930° C for 6 h	
G	$Pb_{0.99}[(Zr_{0.52}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$	0.375 wt % Li–Bi 0.025 wt % Li_2CO_3

stabilized for 24 h. Previous experiments had confirmed that under this poling field the prepared samples which have coercive fields smaller than 1.15 kV mm^{-1}, could be satisfactorily polarized while no failure due to breakdown or microcrack growth occurred. The piezoelectric properties were measured by the resonance method [9]. The dielectric properties of the poled samples were also examined by HP 4270A capacitance bridge.

The basic compositions to be studied were listed in Table I, together with the kind and amount of the additives. These compositions were categorized into seven groups and were denoted by the capital letters from A to G, respectively.

3. Results and discussion

3.1. Selection of doping amount of PZT 52/48

After appropriate sintering process, the dielectric properties of Li–Bi and Na–Bi pair-doped PZT 52/48 are shown in Fig. 1a and Fig. 1b, respectively. Where Li–Bi and Na–Bi stand for the pair doping of monovalent cation Li^+ (or Na^+) with equal mole fraction of trivalent Bi^{3+} and the abscissa shows the weight fractions of monovalent dopants (in carbonate form).

Like the results we obtained previously, [6] a peculiar region at about 0.375 wt % doping amount is observable in Li–Bi doped PZT 52/48. Maximal relative dielectric constant and minimal dissipation factor were found in this region. While no such obvious peculiarity was found in Fig. 1b for Na–Bi pair-doped PZT 52/48. This was reasonable because the ionic radius of Li^+ was smaller (0.068 nm) than that of Pb^{2+} (0.120 nm), so a large possibility of interstitial site-occupancy was expected, while Na^+ (0.095 nm) had less possibility because its radius was larger than that of Li^+. X-ray diffraction analysis also showed a maximum c/a ratio at about 0.375 wt % Li–Bi doping level (not shown here), which confirmed that Li^+ really had the chance to occupy the octahedral interstice. With lithium located at the octahedral interstice, this donor-type doping would increase the resistivity and decrease the dissipation factor of the pair-doped PZT 52/48. In case of Na–Bi pair doping, only a small peak was found at about 0.25 wt % doping level. It was believed that both Na^+ and Bi^{3+} were A-site substitution [10]. This 0.25 wt % doping level was about half of that of the peculiarity took place when only Na_2CO_3 was doped (0.5 wt %), so both Na^+ and Bi^{3+} were believed to be A-site substitution.

When the doping level was beyond 0.5 wt %, the dielectric constant and dissipation factor increased sharply as the consequences of the influence of both solubility limit and B-site substitution, which increased the conductivity due to the occurrence of highly conductive second phase and/or the behaviour of acceptor-type dopings. While in the Li–Bi pair-doping case, the increase in dielectric constant was abated due to the higher solubility and interstitial effect of Li^+. In Fig. 2, there showed the Curie points of Li–Bi doped PZT 52/48 against the doping amounts. It could be seen that the Curie temperature was increased at about 0.375 wt %. This might result from the expansion of the crystal lattice after interstitial occupancy. As stated above, at this doping amount a larger c/a ratio was observed, which enhanced the tetragonality of the crystal lattice and brought an upward shift of the tetragonal–cubic phase boundary and so did the Curie point [11]. Another thing worth mentioning was that Curie points decrease continuously until the doping amount reached about 1.0 wt %. In addition to this, the Curie points of pair dopings were lower than those doped with Li_2CO_3 or Na_2CO_3 only. This was attributed to the larger amount of doping cations, which diffuse into the PZT grains [12]. This result also

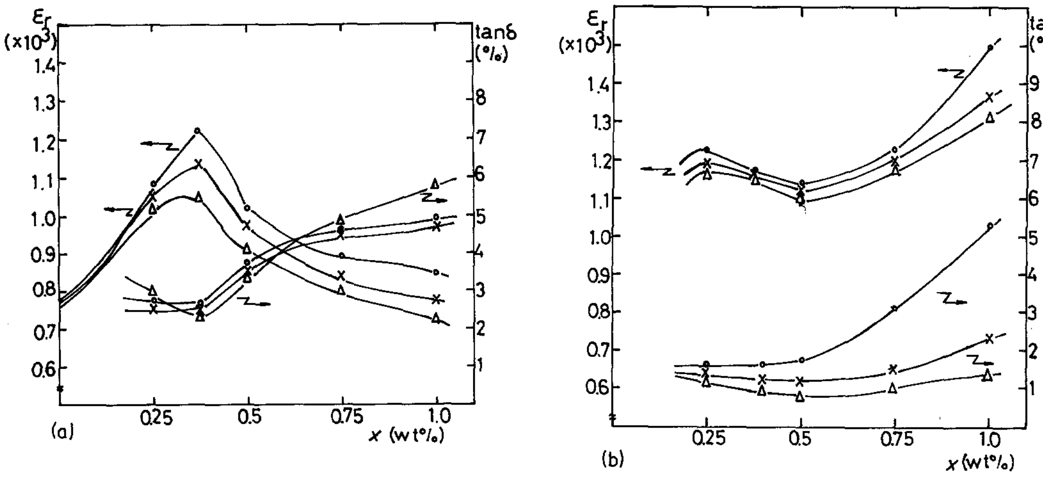


Figure 1 Effect of doping amount on the dielectric properties of (a) Li–Bi doped and (b) Na–Bi doped PZT 52/48. (○) 1 kHz; (×) 10 kHz; (△) 100 kHz.

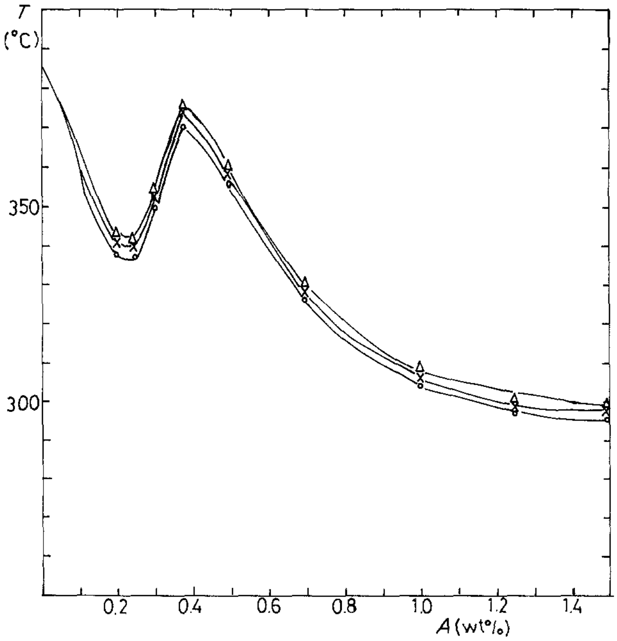


Figure 2 Curie temperatures of Li–Bi doped PZT 52/48. (○) 1 kHz; (×) 10 kHz; (△) 100 kHz.

revealed that the solubility limits of the doped cations were larger in the pair doping case than in the single doping case. The process-sensitive properties of the doped PZT 52/48 could thus be, to some extent, released.

The piezoelectric properties of Li–Bi pair-doped PZT 52/48 are shown in Fig. 3. Again, oddities are found at doping around 0.375 wt %. It could be seen from Fig. 3a that the k_p values of the pair-doped samples did not change that much as those of the single carbonate-doped ones. The peak k_p shifted towards lower doping level as the sintering temperature increased. This implied that the inward diffusion of the doped cations was more effective if the sintering temperature is increased. Peak dielectric constant after poling, ε_{33}^{T}, with a value higher than 1200 was found at the same doping level as that of peak k_p. Increases in Q_m (mechanical quality factor) were observed when the doping amount increased beyond 1.0 wt %, where larger amount of space charges existed [13]. From these figures, one could recognize that the best piezoelectric properties of a pair-doped PZT 52/48, could be obtained with an about 0.375 wt % doping amount, and sintering at 1050 to 1100° C.

3.2. Niobium-modified PZT 52/48

In order to further the applications of this pair-doping, another basic composition $Pb[(Zr_{0.52}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$ (abbreviated as PZTN 52/48) was selected. In preparing this composition, a 0.01 mol % PbO-rich condition existed if the Nb^{5+} is assumed to be located at the B-site of the perovskite lattice, as it was indeed the case, [14] pair doping was applied by adding 0.375 wt % Li–Bi pair into the PZTN 52/48 ceramics. For the purpose of comparison, 0.375 wt % Li–La pair doping was also applied. In the experiments, the amount of Li_2CO_3 was slightly increased to compensate the loss of Li_2CO_3 in sintering process and kept the mole-fraction of Li/Bi close to unity. The amount of this increase was around 0.025 wt %. Furthermore, excess PbO was added deliberately into the composition to study the effect of PbO rich condition on the piezoelectric properties of the pair-doped PZTN 52/48.

Fig. 4 showed the linear shrinkage and density of the pair doped PZTN 52/48. Densification seemed to be accomplished at 950° C sintering temperature. The only exception was for Group E, when the densification was accomplished only after sintering at about 1100° C since the amount of liquid-phase former in group E was smaller. However, all the curves showed the characteristics of liquid-phase sintering [15]. Fig. 4 also showed that the saturated density of Li–Bi pair-doped PZTN 52/48 (curve D) was smaller than that of PZTN 52/48 sintered with 9 wt % PbO (curve B). The dielectric properties of the pair-doped PZTN 52/48 were shown in Fig. 5. A saturated value was approached for each sample when the sintering temperature increased over certain level, which could also be visualized as the indication of whether the sintering was satisfactory or not. In Fig. 5, a high dielectric constant

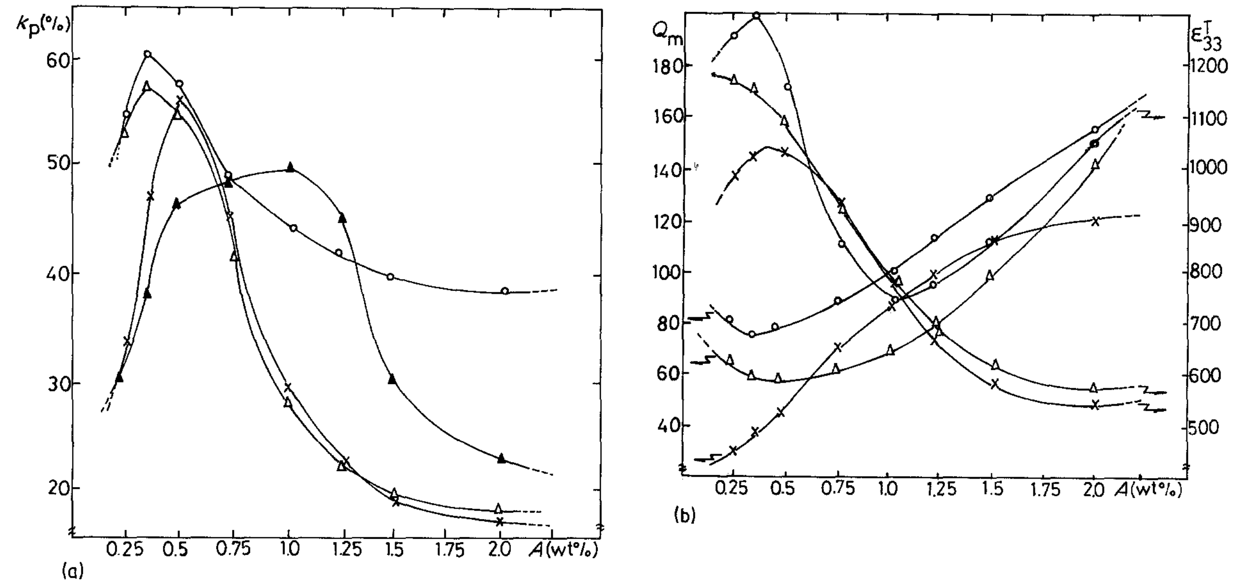


Figure 3 Piezoelectric properties (a) k_p, (b) Q_m and ε_{33}^{T} of Li–Bi doped PZT 52/48 with doping level and sintering temperature as variables. Sintering time was 2 h for each condition. (▲) 950° C; (×) 1000° C; (○) 1050° C; (△) 1100° C.

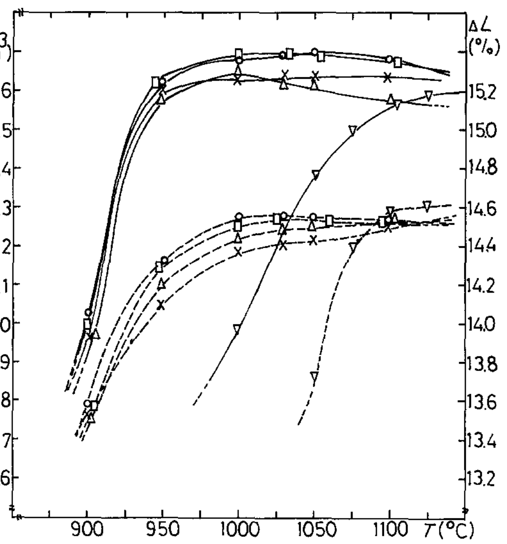


Figure 4 Densities and linear shrinkages of group A to group E. Compositions of each group were listed in Table I. (□) A; (○) B; (△) (×) D; (▽) E; (——) *d*; (– – –) Δ*L*.

was observed for Li–La pair doping, which was similar to the dielectric property of (Pb, La)(Zr, Ti)O_3 (so-called PLZT) ceramics [16].

Fig. 6 showed the dielectric properties of some selected groups. In group B, where 9 wt % of excess PbO was added only, the dielectric constant was decreased when sintering temperature was higher than 1050° C. This phenomenon was improved in the result of group C where 0.375 wt % Li–Bi doped pair was added simultaneously with excess PbO. The improvement was even better in the result of group D, where 0.375 wt % Li–Bi and 0.025 wt % excess Li_2CO_3 were added. The reason of this improvement lay in the diffusion of Li^+ and Bi^{3+} into the PZT grains without excess Pb^{2+}. The lowest dissipation factor, lower than 2%, was also found in group D when the sintering temperature was higher than 1000° C. The curve of group F was the result of group D after annealing at 930° C for 6 h. Almost constant dielectric constants were found in the result of group F between 1000 to 1100° C sintering temperature. However, the dissipation factor was increased here, which was believed due to the driving out of the diffused cations. Anyway, the dielectric properties were quite stable when sintering at temperature between 1000 to 1100° C, if Li–Bi pair-doping was adopted.

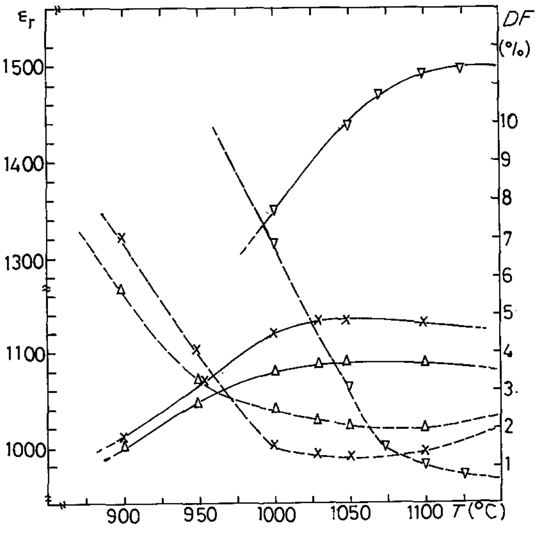


Figure 5 Dielectric properties of group (△) C; (×) D; (▽) E; (——) ε_r; (– – –) *DF*.

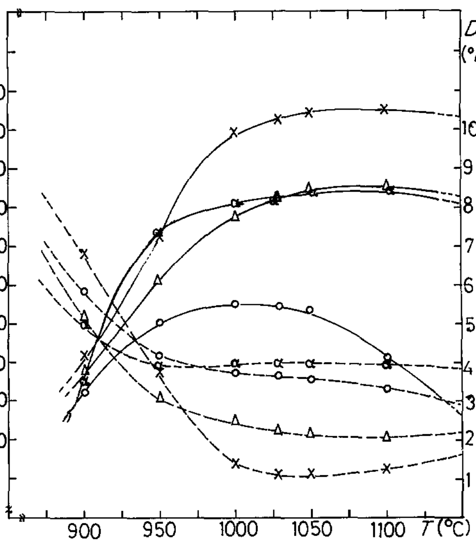


Figure 6 Dielectric properties of group (○) B, (△) C, (×) D; (α) F; (——) ε_r; (– – –) *DF*.

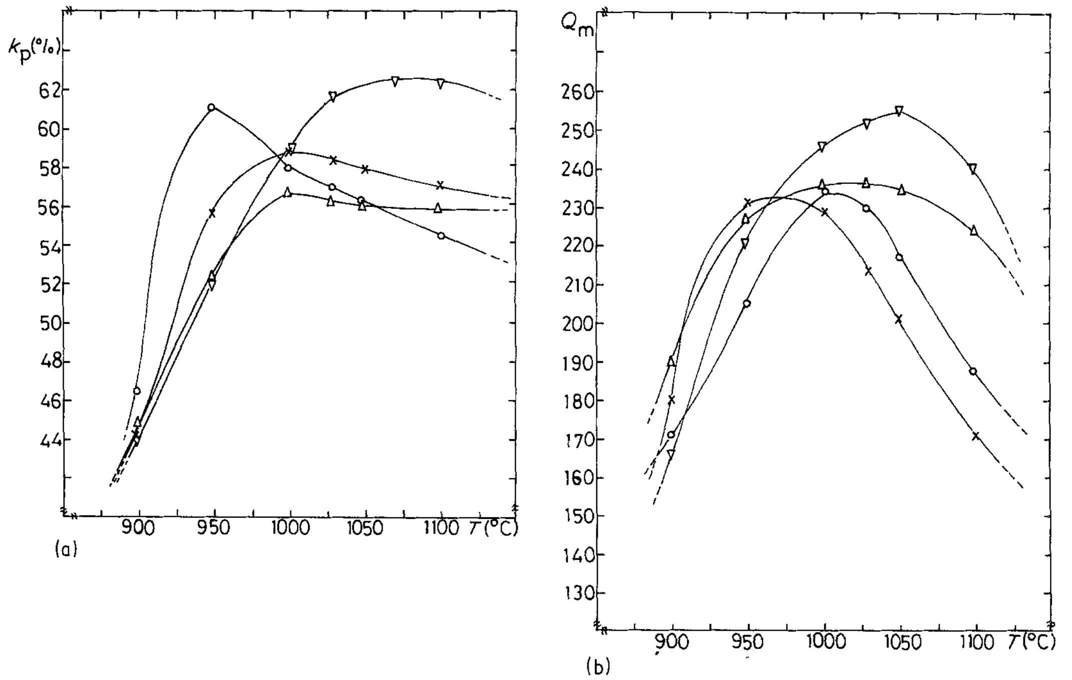
The piezoelectric properties were shown in Fig. 7 where group G representing PZTN 52/48 doped with 0.375 wt % Li–Bi and 0.25 wt % Li_2CO_3 but with deficient PbO content was elucidated for comparison. Also, an almost constant value was approached for each group after sintering at temperature above 1000° C. Comparatively speaking, if the samples were sintered at temperature between 1000 to 1100° C, process-insensitive piezoelectric properties, just like those of dielectric properties, were obtained. It could also be seen from Fig. 7 that k_p values ranging from 56 to 62%, frequency constant *N* around 1720 kHz mm (Fig. 7a), maximal Q_m as high as 250 and dielectric constant after poling ε_{33}^T about 1050 (Fig. 7b) could be achieved by 1050° C sintering. The advantages of pair-doping process would be more clear by comparing the piezoelectric properties of the pair-doped PZTN 52/48 with those of PZT 52/48 (Figs 9 and 10 of [6]).

3.3. PbO-deficient PZTN 52/48

It was known that the vapour pressure of PbO affected the piezoelectric properties of PZT ceramics to a great extent, [17] and usually excess PbO was provided for compensation [18]. The intention here was to investigate the effect of PbO amount on the properties of PZTN 52/48 under pair-doping conditions.

As listed in Table I, group B and C consisted of 9 and 3 wt % excess PbO, respectively, and group D had pair doping only. In group G, where the content of PbO was deliberately reduced and the composition was fabricated as $Pb_{0.99}[(Zr_{.052}Ti_{0.48})_{0.98}Nb_{0.02}]O_3$, with PbO deficient by 1 mol % or 0.64 wt %. Consequently, if the composition groups were listed sequentially according to the contents of PbO, the first would be group B, then group C, group D and A, and lastly the PbO-deficient case of group G.

No obvious difference of the sintering behaviour between these groups were observed in Fig. 4, they all



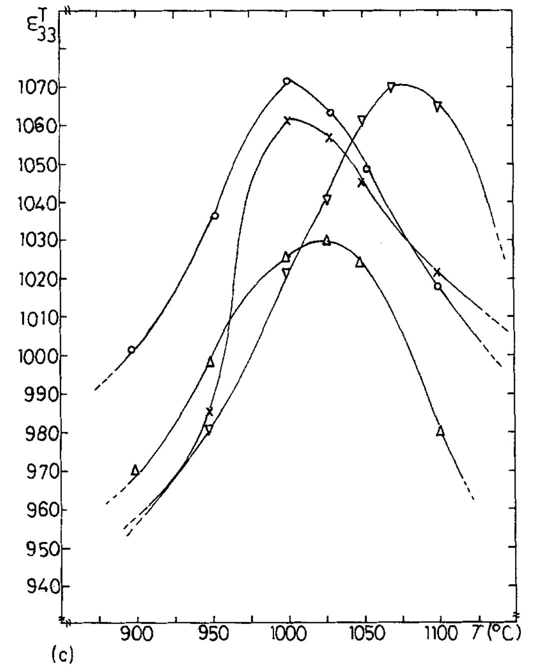


Figure 7 (a) k_p, (b) Q_m and (c) ε_{33}^T of group (△) C; (×) D; (○) F; (▽) G.

were densified completely at temperature around 1000° C. Liquid phases, formed by either the excess PbO or the Li–Bi doping pair, both promoted the sintering of PZTN 52/48. Because excess PbO would drive the crystalline phase of PZT away from the morphotropic phase boundary, deterioration of the electrical properties of the sample with excess PbO was found [19]. The influence could be recognized from the dielectric properties in Figs 5 and 6, and the piezoelectric properties in Fig. 7. According to the results shown in Figs 5 and 6, the better way to improve the dielectric properties of the Li–Bi pair doped PZTN 52/48 was to adopt group D composition rather than group B or C. In other words, excess PbO could do nothing to improve the dielectric properties with the presence of doping pairs. Similarly, in Fig. 7, poorer piezoelectric properties were found in PbO-rich samples. It was the group G, with PbO-deficient composition, had k_p up to about 62%, high N of about 1840 kHz mm, Q_m of about 255 and ε_{33}^T of about 1070. Which was superior to other composition groups. So the electrical properties of the doped PZTN 52/48 could be improved by pair doping and the problem of providing excess PbO for compensation was released in case of pair doping.

4. Conclusions

The electrical characteristics of Li_2CO_3- or Na_2CO_3-added PZT 52/48 could be improved by pair-doping process, i.e. doping equal amount of R^+ and R^{3+} simultaneously, to compensate the unbalanced charges arose from Li^+ or Na^+ doping only. Besides this, the obtained properties of PZT 52/48 could be process-insensitive with the pair dopings.

Pair-doping method could be applied to PZTN 52/48 with good results. After appropriate sintering process, together with the Li–Bi pair doping, the obtained planar coupling factor was as high as 62%, frequency constant N around 1840 kHz mm, mechanical quality factor Q_m of about 255, and the dielectric constant after poling ε_{33}^T of about 1070. Where similar process-insensitive properties were obtained.

Pair-doping method could also release the problem of excess PbO added in sintering for compensation. In Li–Bi pair-doped PZTN 52/48, better dielectric and piezoelectric properties were obtained with PbO-deficient rather than PbO-rich composition. From the results obtained above, the optimal sintering conditions were at 1050° C for 2 h, and when the pair-doping process was adopted, excess PbO for compensation was not required.

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