Effects of atmospheric powder on microstructure and piezoelectric properties of PMZN-PZT quaternary ceramics

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Abstract

The effects of atmospheric powder on microstructure and piezoelectric properties of $Pb(Mn_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ (PMZN-PZT) quaternary ceramics were investigated. Specimens with various contents of $Pb(Mn_{1/3}Nb_{2/3})O_3$ from 0 to 20 mol% were prepared by columbite two-stage process with and without atmospheric powder of $PbZrO_3$. The results revealed that the atmospheric powder is favored to the liquid-state sintering process in PbO vapor pressure equilibrium. The specimen sintered with atmospheric powder is homogenous and the fracture is intergranular. However, the specimen sintered without atmospheric powder is less homogenous and the fracture is essentially transgranular. On the other hand, the pyrochlore phase was formed along with the perovskite phase for the specimens sintered without atmospheric powder and the second phase was seriously detrimental to the electromechanical properties. The superior piezoelectric properties were observed for the specimens sintered with atmospheric powder. By optimizing the specimen composition, excellent piezoelectric, and dielectric properties ($Q_m = 2528$, $K_p = 0.55$, $\tan \delta = 0.003$) were obtained at 10 mol% $Pb(Mn_{1/3}Nb_{2/3})O_3$.
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1. Introduction

Recently, the applications of piezoelectric ceramics for piezoelectric transformers were vigorously studied for lighting liquid-crystal display (LCD) backlights.[1,2] The properties of these materials should combine a high mechanical quality factor (Q_m) with high electromechanical coupling factor (K_p) and low dielectric loss ($\tan \delta$) simultaneously because the piezoelectric transformer operated at its resonant frequency in transformation between electrical and mechanical energy.[3] It is well known that $Pb(Mn_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ (PMZN-PZT) quaternary ceramics are good candidates for piezoelectric transformer due to their superior piezoelectric properties.[4] However, a major problem encountered in the course of ceramics fabrication is the necessary control of lead oxide content during sintering. The loss of PbO and the resultant variation in composition affect greatly the

piezoelectric characteristics.[5,6] Therefore, it is necessary to adjust the vapor phase equilibrium of PbO between the ceramic to be sintered and the atmospheric powder in which the ceramic is embedded.

Until now, there are many reports on the effects of excess PbO in initial raw materials on the structure and electrical properties of lead based ceramics,[7–9] but few on the effects of atmospheric powder such as $PbZrO_3$. Therefore, it is necessary to clarify the relationship between atmospheric powder and the structure and electrical properties of lead based ceramics. In the present work, the variation in structure of PMZN-PZT with respect to the use of atmospheric powder has been investigated. The effect of atmospheric powder on the piezoelectric and dielectric properties also has been measured and correlated with the structure of the materials.

2. Experimental procedures

The general formula of the materials studied was $(Pb_{0.995}Sr_{0.005})(Mn_{1/3}Nb_{2/3})_x (Zn_{1/3}Nb_{2/3})_{0.20-x}Ti_{0.42}Zr_{0.38}O_3 + 1.5\,wt.\%\,PbO + 0.20\,wt.\%\,CeO_2$, where $x = 0, 0.05, 0.10,$
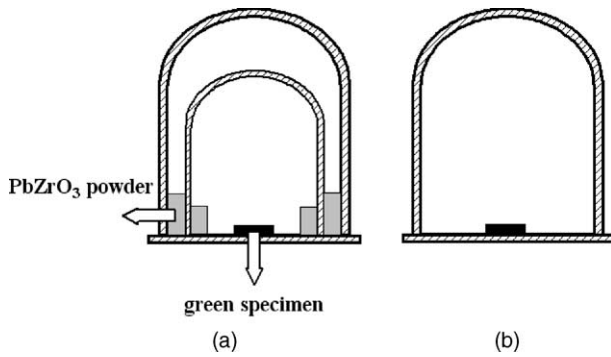
Fig. 1. Sintering alumina crucible configurations: (a) double enclosed alumina crucible method, (b) single enclosed alumina crucible method.

0.15, and 0.20, respectively. The samples were prepared by the columbite two-stage method.[10] Appropriate amounts of prefabricated columbite precursor, $ZnNb_2O_6$ and $MnNb_2O_6$, were mixed with Pb_3O_4, ZrO_2, TiO_2, $SrCO_3$, and CeO_2 by ball-milling with zirconia balls media. The mixture was then calcined at $850\,^{\circ}C$ for 2 h in air, remilled, pressed into discs at around 120 MPa. The green discs were then sintered at $50\,^{\circ}C$ temperature intervals between 1150 and $1350\,^{\circ}C$ for

2 h. In order to investigate the effect of atmospheric powder of $PbZrO_3$, the two compared sintering configurations used identical alumina crucible as shown in Fig. 1 were selected: double enclosed alumina crucible method (Fig. 1(a)), where the green specimens were surrounded with atmospheric powders of $PbZrO_3$ and kept inside the double enclosed alumina crucibles; single enclosed alumina crucible method (Fig. 1(b)), where no atmospheric powders were used and the green specimens were fired directly in a single sealed alumina crucible.

The sintered discs were lapped and electroded with a silver paste. The specimens for the piezoelectric property measurements were poled in a silicone oil bath at $120\,^{\circ}C$ by applying a dc electric field of 3 kV/mm for 30 min.

The crystal structures of the samples were analyzed using an X-ray diffractometry (XRD; Model DMX-IIIC, Japan) with a 2θ range from 15 to 70°. The bulk density was measured using the Archimedean method. Microstructures of the fracture surfaces were examined using a scanning electron microscopy (SEM; Model Hitachi S-570, Japan). The dielectric and piezoelectric properties were measured with an impedance analyzer (Model HP4194A, Hewlett–Packard, CA).
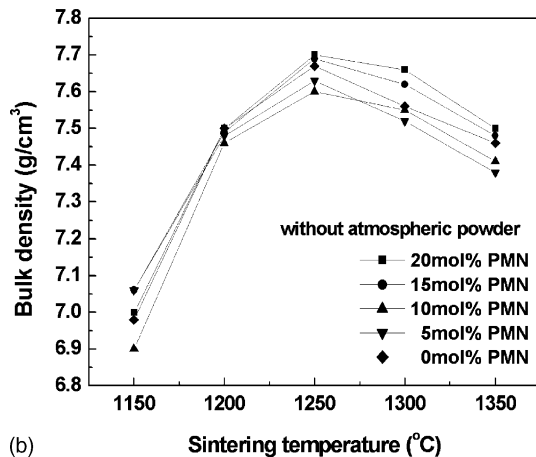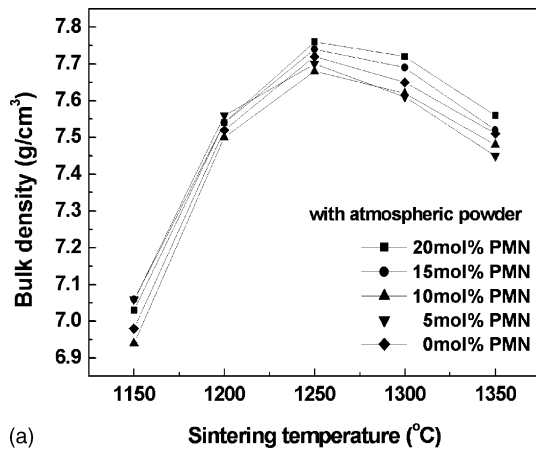

Fig. 2. The bulk density of PMZN-PZT specimens as a function of sintering temperature: (a) with atmospheric powders, (b) without atmospheric powders.
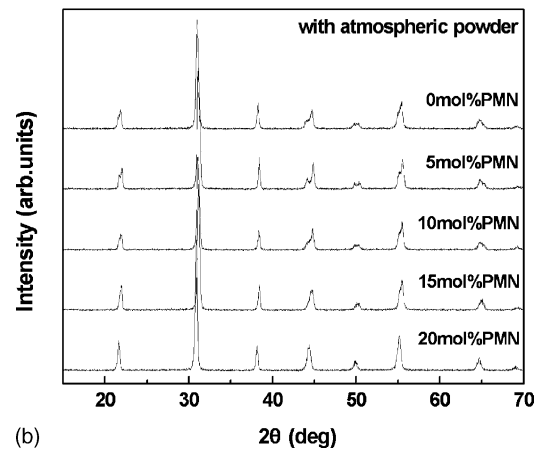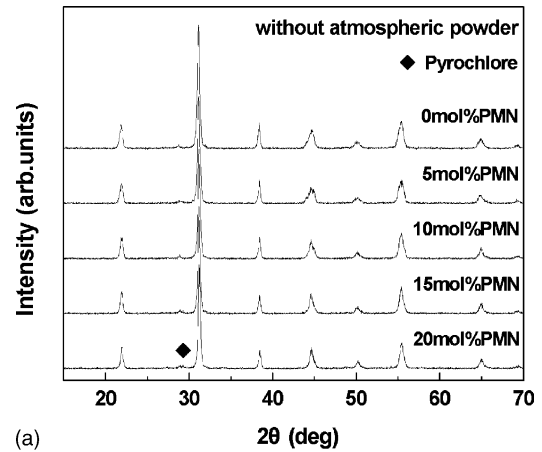

Fig. 3. The XRD patterns of the PMZN-PZT specimens sintered at $1250\,^{\circ}C$: (a) without atmospheric powders, (b) with atmospheric powders.

3. Results and discussion

The bulk densities of PMZN-PZT specimens, sintered with and without atmospheric powders, as a function of sintering temperature are shown in Fig. 2(a) and (b), independently. It can be seen both curves show the similar variation trend with increasing sintering temperature and the maxi-

mum densities are reached at 1250 °C, which gives the optimum sintering condition. In addition, due to the higher weight loss of PbO for none protected specimens, the density of specimens sintered without atmospheric powders is slightly lower than that sintered with atmospheric powders.

The XRD patterns of the PMZN-PZT specimens sintered at 1250 °C with and without atmospheric powders are shown
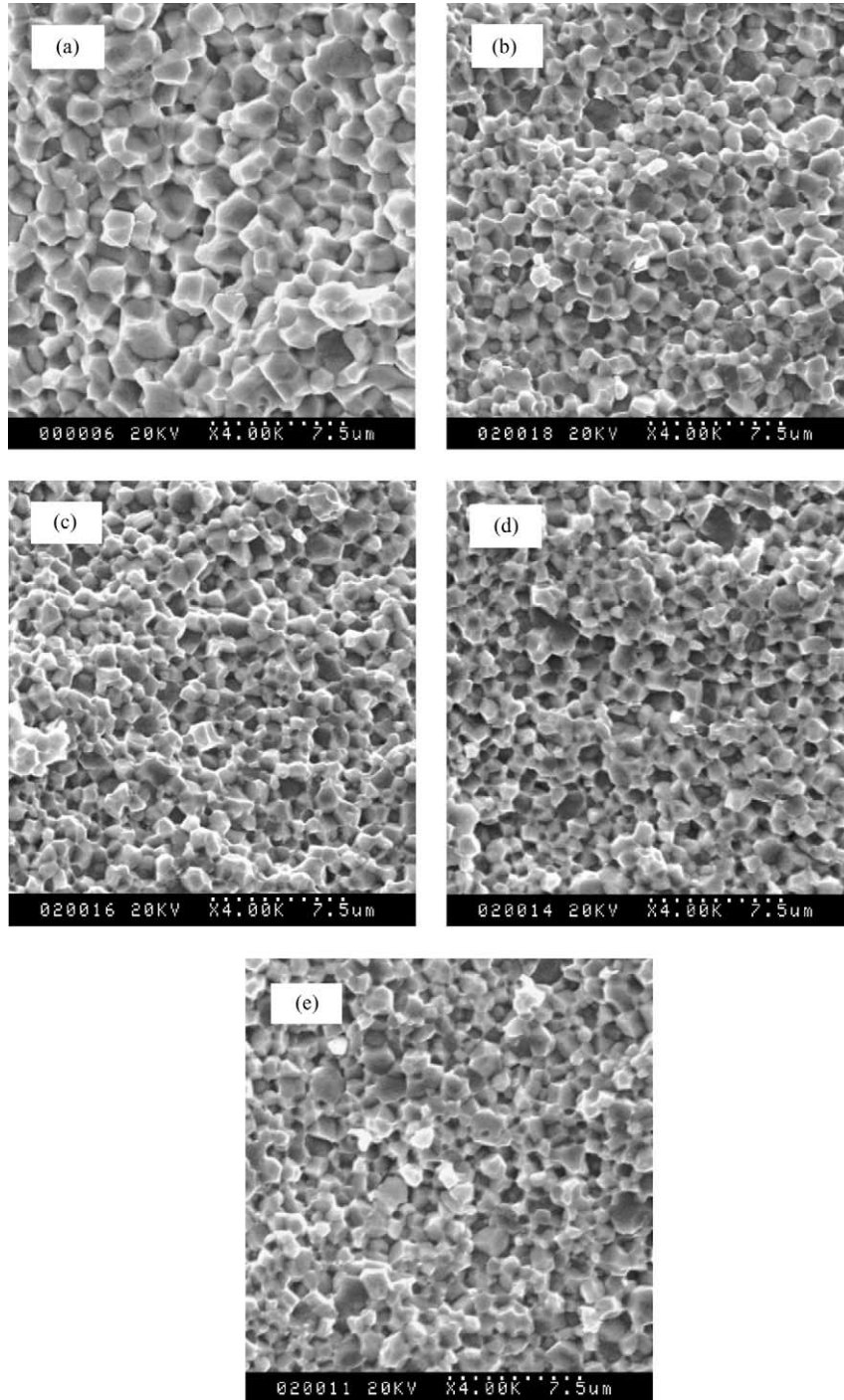

Fig. 4. SEM photographs of the PMZN-PZT specimens sintered at 1250 °C: (a) 0 mol%, (b) 5 mol%, (c) 10 mol%, (d) 15 mol%, and (e) 20 mol% $Pb(Mn_{1/3}Nb_{2/3})O_3$ with atmospheric powders; (f) 0 mol%, (g) 5 mol%, (h) 10 mol%, (i) 15 mol%, and (j) 20 mol% $Pb(Mn_{1/3}Nb_{2/3})O_3$ without atmospheric powders.
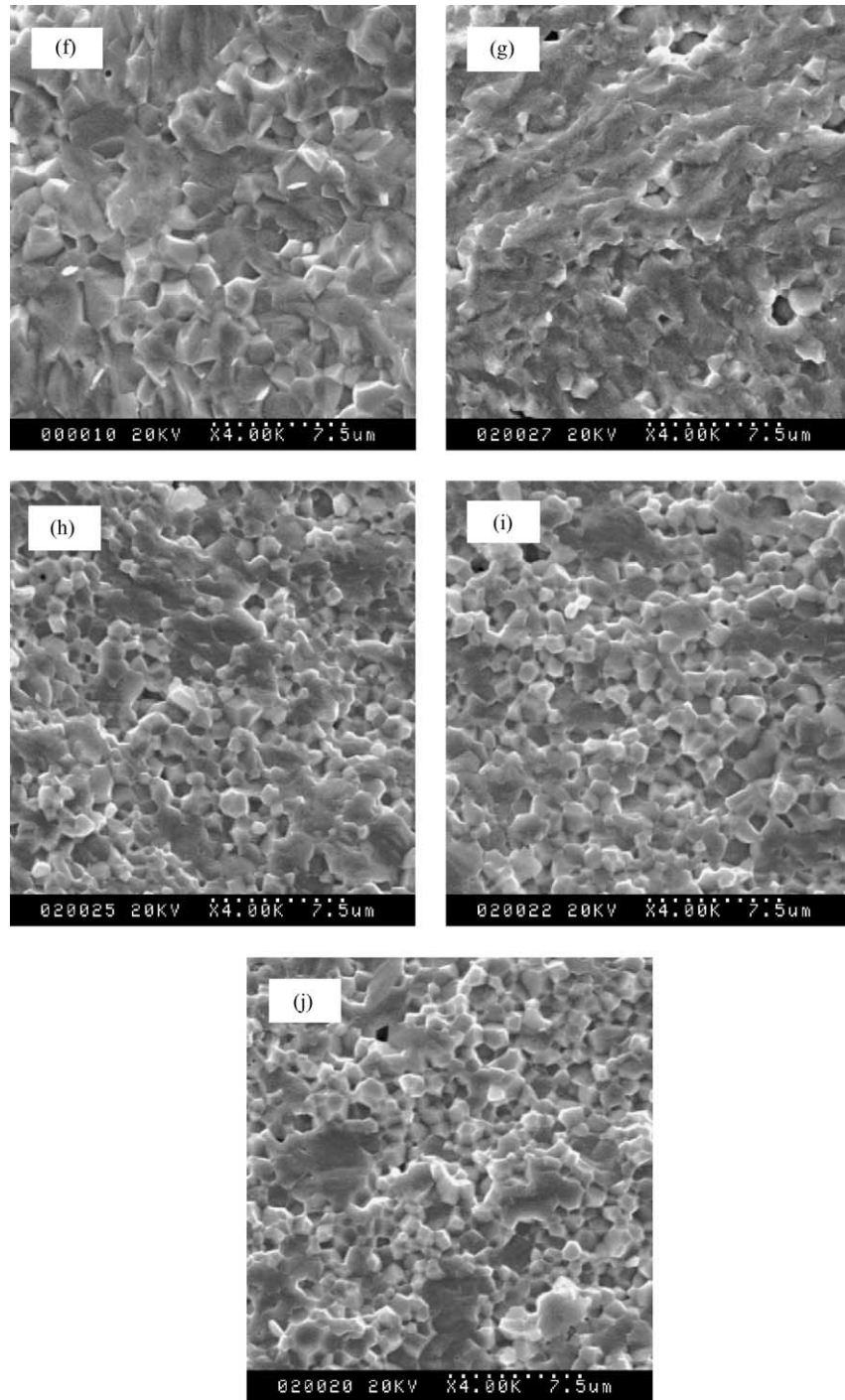
Fig. 4. (*Continued*).

in Fig. 3(a) and (b), independently. Although the columbite method is utilized to synthesize the present materials, a single phase structure of PMZN-PZT specimens sintered without atmospheric powder is not obtained, where some pyrochlore secondary phase is observed (Fig. 3(a)). The reason is probably because of the deviation from the stoichiometry by lead loss when the specimens sintered in high sintering temperature without protected atmospheric powder. Compared with Fig. 3(a), only pure perovskite phase existed and

no pyrochlore phase can be detected in Fig. 3(b). The results attributed to the weight loss of the specimens during sintering was negligible (<0.5 wt.%) because of the use of the $PbZrO_3$ powder atmosphere.

Strong differences in the microstructure of the PMZN-PZT specimens sintered at 1250 °C with and without atmospheric powders are evidenced by the SEM photographs shown in Fig. 4. It is evidenced that the specimen sintered with atmospheric powder is homogenous and the fracture
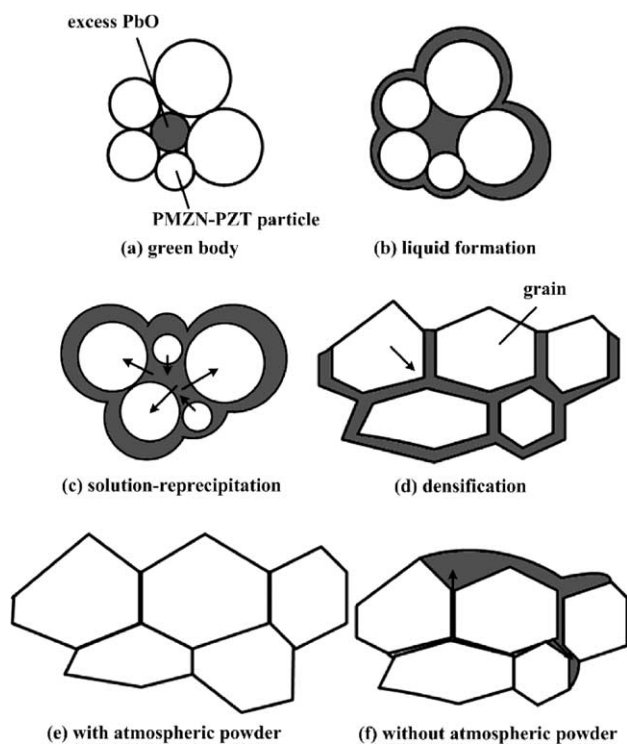
Fig. 5. Scheme of the sintering behavior of the PMZN-PZT specimens.

Fig. 6. The room-temperature dielectric constant (ε_r) of PMZN-PZT sintered at 1250 °C with and without atmospheric powders as a function of $Pb(Mn_{1/3}Nb_{2/3})O_3$ content.

is intergranular. In contrast, the specimen sintered without atmospheric powder is less homogenous and the fracture is essentially transgranular. The differences in microstructure between two sets of specimens can be explained taking into account the different sintering scheme, as shown in Fig. 5. First, the liquid phase is formed in a localized region with high PbO concentration (Fig. 5(a) and (b)). The liquid source in the PbO-rich disk is the excess PbO. The small particles then dissolve in the liquid and reprecipitate on larger grains (Fig. 5(c)). The liquid wets and covers the surface of grains and the densification is promoted by liquid phase sintering (Fig. 5(d)). In the final stage of the sintering, most amount of the liquid phase reabsorbed into the grains (Fig. 5(e)). The above presented scheme only refers to the sinter process with atmospheric powder. As PbO has low melting point of 850 °C, it tends to evaporate in high sintering temperature. When the $PbZrO_3$ atmospheric powder is used, the evaporation of PbO is suppressed. This attributed to the established equilibrium of PbO vapor pressure between the PMZN-PZT compact and $PbZrO_3$ atmospheric powder. However, when the $PbZrO_3$ atmospheric powder is not used in the sintering process, PbO will flow from the compact to the exterior greatly. So, in the final stage of the sintering, PbO-rich amorphous phase is formed in the grain boundary and ceramic surface (Fig. 5(f)). The amorphous phase results in the reduction of the local stress in grains and thus the fracture of the sintered compact is transgranular.

Except of the change in microstructure, atmospheric powder also affects significantly the dielectric and piezoelectric properties of PMZN-PZT ceramics. The room-temperature
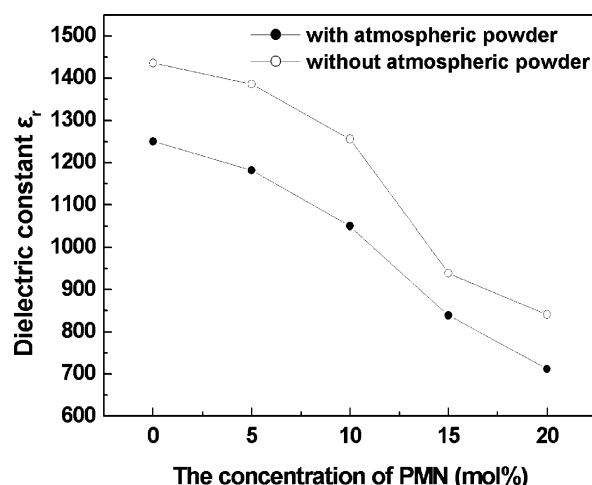
dielectric constant (ε_r) and electromechanical coupling factor (K_p) of PMZN-PZT sintered at 1250 °C with and without atmospheric powders as a function of $Pb(Mn_{1/3}Nb_{2/3})O_3$ content are plotted in Figs. 6 and 7, independently. It can be seen that both ε_r and K_p decreases monotonically with increasing $Pb(Mn_{1/3}Nb_{2/3})O_3$ content. $Pb(Mn_{1/3}Nb_{2/3})O_3$ has little solubility (<5 mol%) in the PZT composition matrix and excess $Pb(Mn_{1/3}Nb_{2/3})O_3$ beyond the solubility limit is believed to segregate at grain boundaries,[3] which leads to the increase in the extent of space–charge polarization at the grain boundaries, resulting in domains bound within grains and decrease of ε_r and K_p. In addition, it can clearly be seen from Figs. 6 and 7 that both ε_r and K_p of PMZN-PZT sintered without atmospheric powders are larger than that sintered with atmospheric powders for the same composition. It was assumed that PbO-rich amorphous
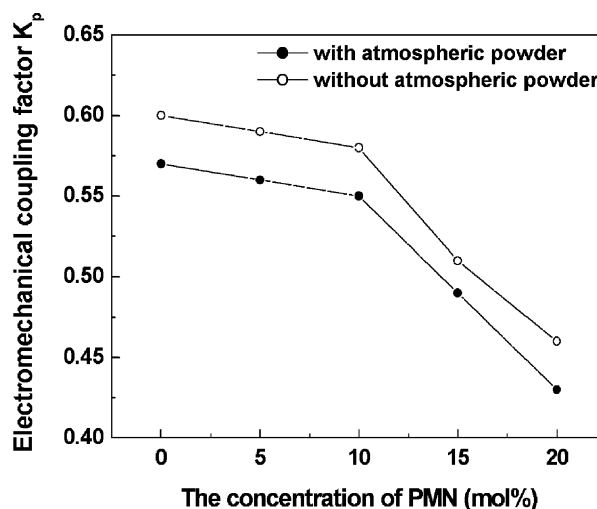

Fig. 7. The room-temperature electromechanical coupling factor (K_p) of PMZN-PZT sintered at 1250 °C with and without atmospheric powders as a function of $Pb(Mn_{1/3}Nb_{2/3})O_3$ content.
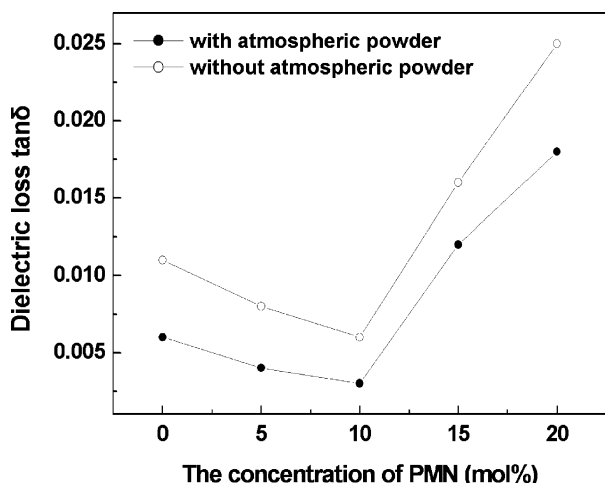
Fig. 8. The room-temperature dielectric loss ($\tan\delta$) of PMZN-PZT sintered at $1250\,^{\circ}\mathrm{C}$ with and without atmospheric powders as a function of $\mathrm{Pb(Mn_{1/3}Nb_{2/3})O_3}$ content.

phases in grain boundaries, for the specimens sintered without $\mathrm{PbZrO_3}$ atmospheric powders, reduce the local stress in domains and facilitate the domain switching, thus both ε_r and K_p increase.

Figs. 8 and 9 give the room-temperature dielectric loss ($\tan\delta$) and mechanical quality factor (Q_m) of PMZN-PZT sintered at $1250\,^{\circ}\mathrm{C}$ with and without atmospheric powders as a function of $\mathrm{Pb(Mn_{1/3}Nb_{2/3})O_3}$ content, independently. It is evident that both curves show the similar tendency that the value of Q_m or $\tan\delta$ of PMZN-PZT specimens sintered with $\mathrm{PbZrO_3}$ atmospheric powders is superior than that sintered without $\mathrm{PbZrO_3}$ atmospheric powders. The above variations of Q_m and $\tan\delta$ are different from ε_r and K_p shown in Figs. 6 and 7. It is assumed that both amorphous phase and pyrochlore phase of specimens sintered without atmospheric powders deteriorated Q_m and $\tan\delta$. Moreover,
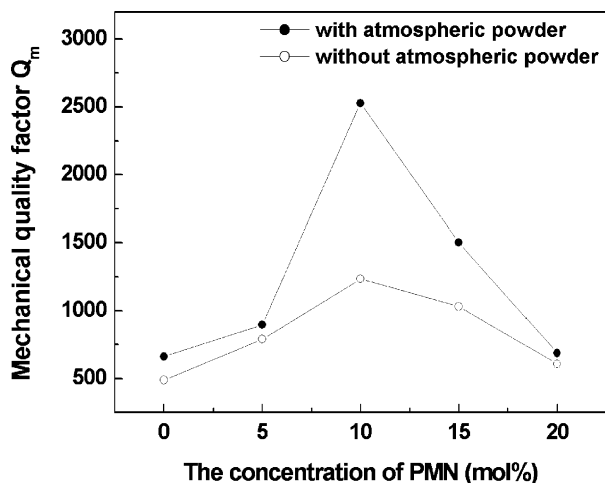
to achieve the piezoelectric transformer transferring high power, it is necessary have a high mechanical quality factor, Q_m and low dielectric loss, $\tan\delta$ because the piezoelectric transformer operated at its resonant frequency under a high input voltage leads to the temperature rise and the deterioration of piezoelectric properties with the increase of its vibration velocity. By adjusting the composition, the excellent values of Q_m (2528) and $\tan\delta$ (0.003) were obtained at 10 mol% $\mathrm{Pb(Mn_{1/3}Nb_{2/3})O_3}$ with protected atmospheric powder, which is promising as an optimal material for high power piezoelectric transformer.

4. Conclusions

PMZN-PZT ceramics sintered with and without $\mathrm{PbZrO_3}$ atmospheric powders were investigated to determine the composition for optimum piezoelectric properties. The results revealed that the atmospheric powders facilitated the sintering process in lead rich atmosphere, so the weight loss of the specimens was negligible and the pure perovskite phase was acquired. However, when the specimens were sintered without atmospheric powders, the loss of PbO from the compact to the exterior leads to the formation of pyrochlore phase and amorphous phase, which deteriorated the properties of Q_m and $\tan\delta$. It should be pay more attention that in the lead rich atmosphere by the use of atmospheric powders, the composition containing 10 mol% $\mathrm{Pb(Mn_{1/3}Nb_{2/3})O_3}$ gave the desirable piezoelectric properties, i.e. Q_m (2528), $\tan\delta$ (0.003), K_p (0.55) and which is a good candidate for piezoelectric transformer application.

Fig. 9. The room-temperature mechanical quality factor (Q_m) of PMZN-PZT sintered at $1250\,^{\circ}\mathrm{C}$ with and without atmospheric powders as a function of $\mathrm{Pb(Mn_{1/3}Nb_{2/3})O_3}$ content.

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