

Effect of Li_2CO_3 addition on the sintering behavior and physical properties of PZT-PZN-PMnN ceramics

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Abstract: The $0.8\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3-0.125\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.075\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3 + x \text{ wt}\% \text{Li}_2\text{CO}_3$ ceramics (PZT-PZN-PMnN), where $x = 0 \div 1.0$, has been prepared by two-stage calcinations method. The Li_2CO_3 addition significantly improved the sinterability of the ceramics, resulting in a reduction of sintering temperature from 1150°C to 930°C . The effect of the Li_2CO_3 addition on the sintering behavior and physical properties of ceramic samples have been investigated. Experimental results showed that all samples have pure perovskite phase with tetragonal structure, the c/a ratio increases with increasing of Li_2CO_3 content. At $x = 0.7$, electrical properties of ceramics are best: the density (ρ) of 7.86 g/cm^3 , the electromechanical coupling factor, $k_p = 0.64$ and $k_t = 0.51$, the dielectric constant, $\epsilon = 1320$, the dielectric loss ($\tan\delta$) of 0.005 , the mechanical quality factor (Q_m) of 1150 , the piezoelectric constant (d_{31}) of 145 pC/N , and the remanent polarization (P_r) of $30.5 \mu\text{C/cm}^2$, which makes it as a promising material for high power piezoelectric devices.

Keywords: Crystal Structure, Dielectrics, Piezoelectrics, Electromechanical Coupling Factor, Li_2CO_3 Addition

1. Introduction

Last several decades have extensive study on the relaxor ferroelectrics since their discovery by Smolenskii *et al.* [1], owing to their significant technical importance on the application of electromechanical devices such as multilayer ceramic capacitors, electrostrictive transducers, micro-displacement positioners. As $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMnN), $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) is a member of lead-based relaxor ferroelectric family with different cations on the B-site of perovskite lattice. These ferroelectric materials have characteristics as high dielectric constant, the temperature at the phase transition point between the ferroelectric and paraelectric phase are broad (the diffuse phase transition) and a strong frequency dependency of the dielectric properties. Gao Feng *et al.* [2] investigated $0.8\text{PZT} - (0.2-x)\text{PZN} - x\text{PMnN}$ ceramics with compositions close to the morphotropic phase boundary (MPB). The optimized values of k_p (0.57), ϵ (842) and Q_m (1020) were obtained at $0.075 \text{ mol Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, which is a new promising material for piezoelectric transformer. However, the sintering temperature of PZT-based ceramics is usually too high, approximately 1200°C [2,3,4,5]. In order to reduce the sintering temperature at which satisfactory densification could be obtained, various material processing methods such

as the 2-stage calcination method [6], high energy mill [7] and liquid phase sintering [6,8,9,10] have been performed. Among these methods, liquid phase sintering is basically an effective method for aiding densification of specimens at low sintering temperature. H. Han *et al.* [9] showed that $0.1 \text{ wt}\% \text{Li}_2\text{CO}_3$ was quite effective in lowering the sintering temperature of PMN-PFN-PZT ceramics from 1100°C down to 900°C , with the retention of good piezoelectric properties. Yu-Dong Hou *et al.* also showed that Li_2CO_3 could increase the piezoelectric properties and reducing the sintering temperature of $0.5\text{PZT}-0.5\text{PZN}$ ceramics from 1100°C down to 950°C [10]. The research results of the above authors clearly showed the significance of Li_2CO_3 addition in controlling the sintering behavior and the electrical properties of the PZT-based ceramics.

Recently, we studied the effect of Zr/Ti ratio content on some physical properties of $0.8\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 - 0.125\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.075\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [11]. We found that the k_p , d_{31} and Q_m of the ceramics are enhanced with the increase of Zr/Ti ratio. At Zr/Ti ratio of $48/52$, the ceramics has the optimal electromechanical properties, $k_p = 0.62$, $d_{31} = 140 \text{ pC/N}$, $Q_m = 1112$. In this study, we investigated the effect of Li_2CO_3 addition on the sintering behavior and physical properties of the PZT-PZN-PMnN ceramics.

2. Experimental Procedure

The general formula of the studied material was $0.8\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3-0.125\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.075\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3 + x \text{ wt}\% \text{Li}_2\text{CO}_3$ (PZT-PZN-PMnN), where x is 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1 and are denoted by M0, M1, M2, M3, M4, M5, M6, respectively. Reagent grade oxide powders (purity $\geq 99\%$) of PbO , ZnO , MnO_2 , Nb_2O_5 , ZrO_2 , TiO_2 and Li_2CO_3 were used as starting materials. Firstly, the powders of $(\text{Zn,Mn})\text{Nb}_2(\text{Zr,Ti})\text{O}_6$ were prepared by reactions of ZnO , MnO_2 , Nb_2O_5 , ZrO_2 and TiO_2 at temperature 1100°C for 2 h. Then $(\text{Zn,Mn})\text{Nb}_2(\text{Zr,Ti})\text{O}_6$ and PbO were weighed and milled for 8 h. The powders were calcined at temperature 850°C for 2 h, producing the PZT-PZN-PMnN compound. Thereafter, predetermined amounts of Li_2CO_3 were mixed with the calcined PZT-PZN-PMnN powder, and then, powders milled for 16h. The ground materials were pressed into disk 12mm in diameter and 1.5mm in thick under 100MPa. The samples were sintered in a sealed alumina crucible with PbZrO_3 coated powder at 870°C , 900°C , 930°C , 950°C and 1000°C for 2 h (M0 sample were sintered to 1150°C).

The crystal structure of the sintered samples were examined by X-ray diffraction (XRD, D8 ADVANCE). The densities of samples were measured by Archimedes method. The ceramic samples were poled in a silicone oil bath at 120°C by applying dc field of 30 kVcm^{-1} for 20 min then cooling under the same electric field. They were aged for 24 h prior to testing.

The piezoelectric properties were determined from the resonance and antiresonance frequency by using an impedance analyzer Agilent 4196B and RLC HIOKI 3532. The dielectric properties were measured by using RLC HIOKI 3532, the ferroelectric property was measured by Sawyer-Tower method.

3. Results and Discussion

3.1. Effect of Li_2CO_3 Addition on the Sintering Behavior of PZT-PZN-PMnN Ceramics

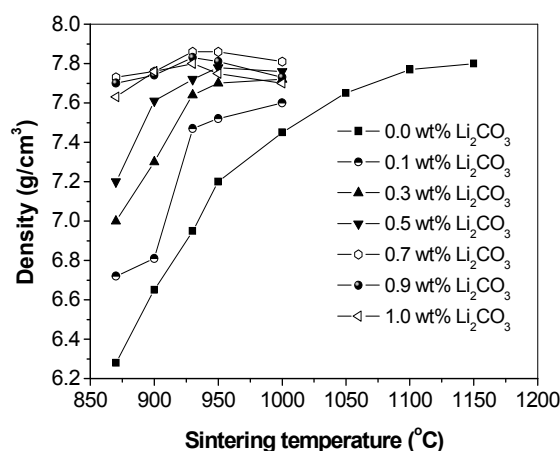


Fig. 1. Density of the PZT-PZN-PMnN + $x\text{wt}\% \text{Li}_2\text{CO}_3$ ceramics as a function of sintering temperature

Fig. 1 shows the variations of density of PZT-PZN-PMnN + $x \text{ wt}\% \text{Li}_2\text{CO}_3$ samples at different sintering temperature. It can be seen that the densities of PZT-PZN-PMnN ceramics change as functions of sintering temperature and the content of Li_2CO_3 sintering aid. Without Li_2CO_3 addition, it is seen that sufficient densification occurs at temperatures 1150°C (the density of 7.82 g/cm^3), while Li_2CO_3 added ceramic samples exhibit densification at a temperature as low as 930°C (the density of 7.86 g/cm^3 at Li_2CO_3 content of 0.7 wt.%), indicating that Li_2CO_3 is quite useful to lower sintering temperature of ceramics, similarly to reports on Li_2CO_3 added PZT-based ceramics [9,10]. When the amount of Li_2CO_3 increase from 0 to 0.7wt%, the density of samples increases with the increasing amount of Li_2CO_3 and the sintering temperature and then decreases.

According to the above results, the optimized sintering temperature of the Li_2CO_3 added PZT-PZN-PMnN ceramics is 930°C . So, the addition of Li_2CO_3 improved the sinterability of the samples and caused an increase in the density at low sintering temperature.

3.2. Effect of Li_2CO_3 Addition on the Structure, Microstructure of PZT-PZN-PMnN Ceramics

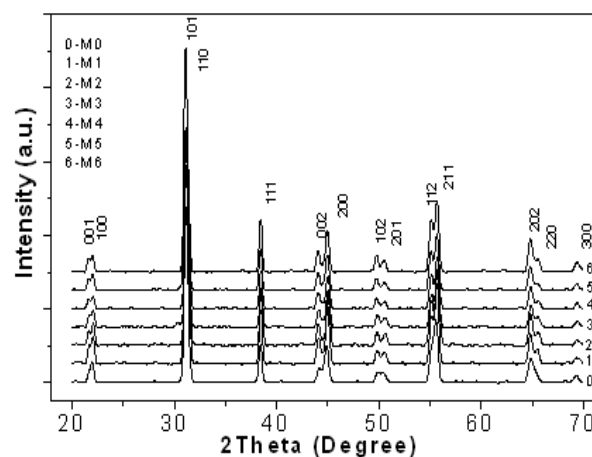


Fig. 2. X-ray diffraction patterns of ceramics with different Li_2CO_3 contents

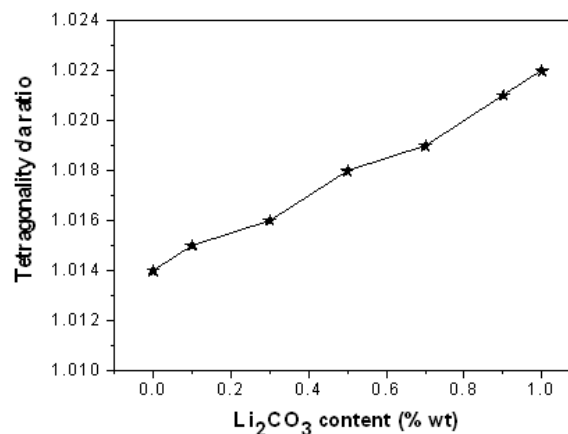


Fig. 3. The tetragonality c/a ratios of ceramics as a function of Li_2CO_3

Fig. 2 shows X-ray diffraction patterns (XRD) of the PZT-PZN-PMnN ceramics at the different concentrations of Li_2CO_3 . All samples have pure perovskite phase with tetragonal structure. When increasing of Li_2CO_3 content, the tetragonality c/a ratio increases as shown in Fig. 3. This can be explained that when Li ions incorporate into the lattice of perovskite structure, they tend to occupy the octahedral sites of the perovskite lattice, forming additional anionic vacancies. This causes a distortion in the lattice, therefore, the substitution of Li^{+1} ions in Ti^{+4} sites let the c -axis be lengthened. These results are consistent with the literature [4].

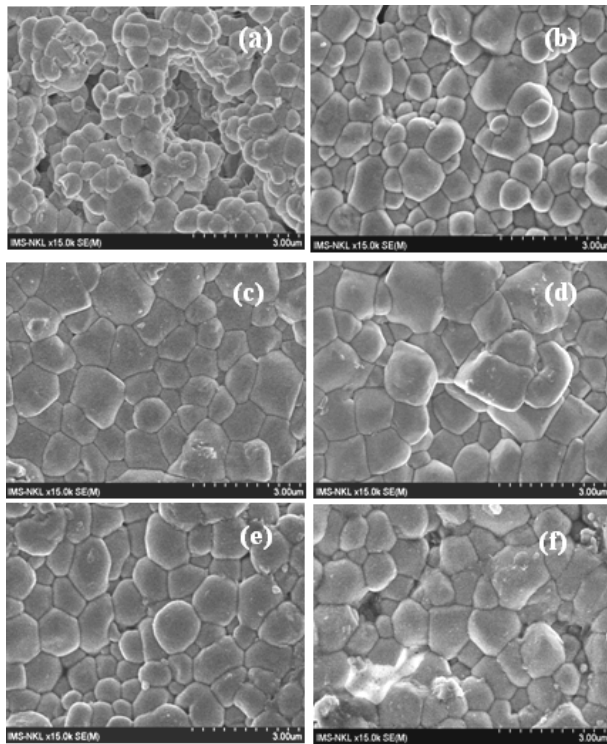


Fig 4. Microstructures of specimens with different amounts of Li_2CO_3 additive sintered at 930°C for 2h: (a) 0 wt%, (b) 0.3 wt %, (c) 0.5 wt %, (d) 0.7 wt %, (e) 0.9 wt % and (f) 1.0 wt %

Fig. 4 shows the SEM images of the fractured surface of PZT-PZN-PMnN ceramic specimens with different amounts of Li_2CO_3 additive sintered at 930°C for 2 h. From fig.4(a), it can be seen that with undoped specimen, the microstructure was inhomogeneous and many distinct pores existed in the grain boundary, which means that the specimen is not sintered effectively, but a uniform and dense microstructure was formed when Li_2CO_3 was added (see Figs. 4(b)–(d)). The average grain size of specimens are increased with the increasing amount of Li_2CO_3 (Fig. 5). This can be explained by liquid phase sintering process. In the initial and intermediate stages of sintering, Li_2CO_3 additives with a low melting point of 720°C [10] forms a liquid phase, which wets and covers the surface of grains, and accelerated the growth of grains [7,8,10]. In the later stage, the Li ions are diffused into the lattice and modify the properties of ceramics. From Fig. 4(e) and 4(f) also shows

that further increasing the Li_2CO_3 content to 0.9 wt % gives rise to an abnormal grain boundary, and the average grain size is reduced. This is mainly attributed to the solubility limit of Li ions in PZT-PZN-PMnN structures. When the addition was above the limit, the excessive Li ions would segregate at grain boundary and inhibit the grain growth [10].

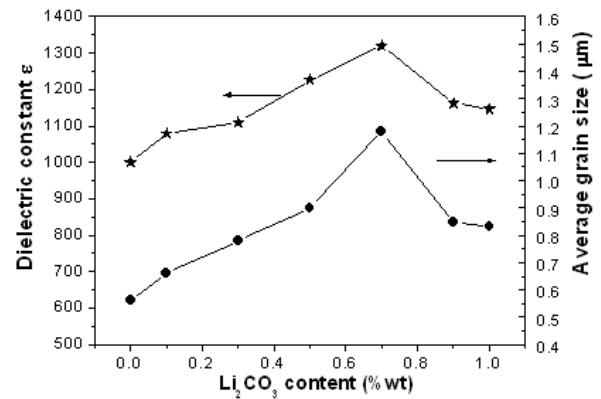


Fig 5. Room-temperature dielectric constant ϵ and average grain size of ceramics with different amounts of Li_2CO_3

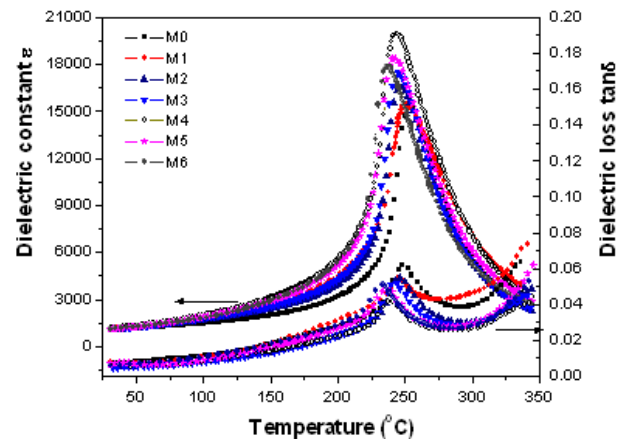


Fig 6. Temperature dependence of dielectric constants and dielectric loss of Li_2CO_3 -doped PZT-PZN-PMnN ceramics at 1 kHz

3.3. Effect of Li_2CO_3 Addition on Physical Properties of PZT-PZN-PMnN Ceramics

The change of Li_2CO_3 content also significantly affect the dielectric, ferroelectric and piezoelectric properties of PZT-PZN-PMnN ceramics.

Fig.5 shows the room temperature dielectric constant ϵ at 1kHz frequency of PZT-PZN-PMnN ceramics as function of the Li_2CO_3 contents. The ϵ increases with the Li_2CO_3 content increases and reaches highest value (1320) at $x = 0.7$. With contents $x > 0.7$, the dielectric constant ϵ decreased. This is related to particle size of ceramics.

Fig. 6 shows the temperature dependence of the dielectric constant ϵ and dielectric loss $\tan\delta$ of PZT-PZN-PMnN ceramics with different amounts of Li_2CO_3 at 1 kHz. As seen, the dielectric properties exhibited characteristics of a relaxor

material in which the phase transition temperature occurs within a broad temperature range. This is one of the characteristics of ferroelectrics with disordered perovskite structure [3]. The maximum dielectric constant ϵ_{\max} increases with increasing Li_2CO_3 content, and at $x = 0.7$ indicated the highest dielectric constant ϵ_{\max} of 20030 and then sharply decreases beyond this point. This can be explained by increasing grain size effect [3,11]. The dielectric loss $\tan\delta$ shows the reversed trend, this agrees with characteristics of dielectrics [3]. From the results in Fig. 6, the Curie temperature T_C of the samples were determined. Corresponding Li_2CO_3 concentration increases from 0 to 1 wt%, Curie temperature of ceramics decreased almost linearly from 253°C to 236°C .

Fig. 7 shows the shape of ferroelectric hysteresis loops of the samples measured at room temperature. From the shape of these loops, the remanent polarization P_r and the coercive field E_c were determined, as shown in Fig. 8. A sharp increase in P_r was observed for M0-M4 samples, reaches the highest value ($30.5 \mu\text{C}/\text{cm}^2$) at $x = 0.7$ (M4), and then decreases. The coercive field E_c decreases slightly with increasing content of Li_2CO_3 and reaches smallest value ($8.7 \text{ kV}/\text{cm}$) at $x = 0.7$. These results are in good agreement with the studied dielectric and piezoelectric properties of the samples.

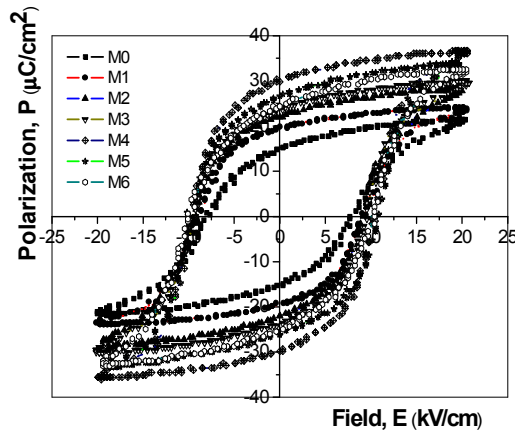


Fig 7. Hysteresis loops of PZT-PZN-PMnN ceramic samples

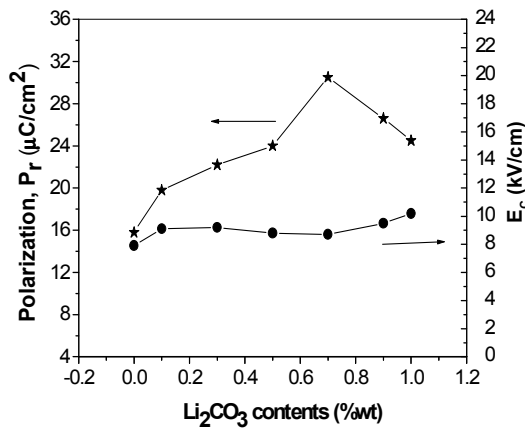


Fig 8. The remnant polarization (P_r) and coercive field (E_c) as a function of the Li_2CO_3 contents

To determine piezoelectric properties of ceramics, resonant vibration spectra of samples were measured at room temperature. From these resonant spectra, piezoelectric parameters of samples were determined.

Fig. 9 shows the electromechanical coupling factor (k_p , k_t), the piezoelectric constant (d_{31}), mechanical quality factor Q_m and dielectric loss $\tan\delta$ change as a function of the amount of Li_2CO_3 . When the amount of Li_2CO_3 is lower than 0.7 wt%, the values of k_p , k_t and d_{31} are rapidly increased with increasing content of Li_2CO_3 , while the mechanical quality factor Q_m and the dielectric loss $\tan\delta$ are lightly decreased. The optimized values for k_p of 0.64, k_t of 0.51, d_{31} of $145 \text{ pC}/\text{N}$, Q_m of 1150 and $\tan\delta$ of 0.005 were obtained at $x = 0.7$. This is probably related to characteristics of the increasing grain size.

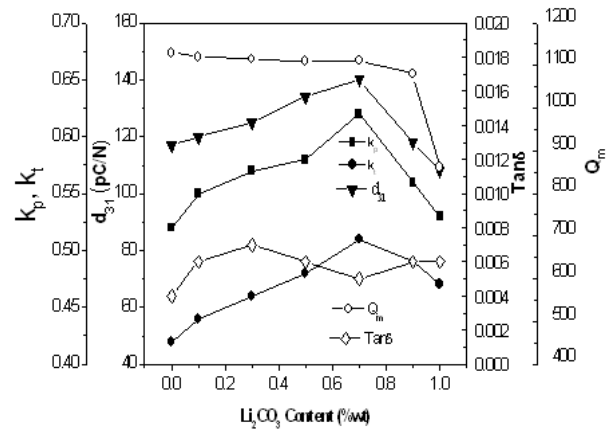


Fig 9. The values k_p , k_t , d_{31} , Q_m , and $\tan\delta$ of the samples

4. Conclusions

Effect of Li_2CO_3 addition on the sintering behavior and physical properties of $0.8\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52}) - 0.125\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3}) - 0.075\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3 + x \text{ wt}\% \text{Li}_2\text{CO}_3$ ($x = 0.0 \div 1.0$) ceramics were investigated. The addition of Li_2CO_3 improved the sinterability of the samples and caused an increase in the density and grain size at low sintering temperature (930°C). All samples have pure perovskite phase with tetragonal structure, the c/a ratio increases with increasing of Li_2CO_3 contents. At the Li_2CO_3 content of 0.7%wt, physical properties of ceramics are best: the density of $7.86 \text{ g}/\text{cm}^3$, the electromechanical coupling factor, $k_p = 0.64$ and $k_t = 0.51$, the dielectric constant, $\epsilon = 1320$, the dielectric loss ($\tan\delta$) of 0.005, the mechanical quality factor (Q_m) of 1150, the piezoelectric constant (d_{31}) of $145 \text{ pC}/\text{N}$, and the remanent polarization (P_r) of $30.5 \mu\text{C}/\text{cm}^2$, which makes it as a promising material for high power piezoelectric devices.

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