

Effects of Complex Additives on Lowering Sintering Temperature and Improving Piezoelectric Properties of PZS-PNT-PZT Ceramics

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Addition of the complex additives $\text{Li}_2\text{CO}_3\text{-Bi}_2\text{O}_3\text{-CdCO}_3$ (LBC) to $\text{PbZn}_{1/3}\text{Sb}_{2/3}\text{O}_3\text{-PbNi}_{1/2}\text{Te}_{1/2}\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PZS-PNS-PZT) composition enhanced the densification rate effectively, meanwhile improved the piezoelectric properties. The complex additives were incorporated as a mill addition to the base PZS-PNS-PZT composition. The optimum sintering temperature was reduced from 1265°C to below 980°C . Effects of composition and addition amount of LBC on sintering temperature and piezoelectric properties have been investigated. The different combinations of LBC show the different effects on the electrical properties and the sintering temperature of PZS-PNT-PZT ceramics. The shrinkage behavior of the samples with LBC was examined by means of isothermal sintering and DTA. The changes in microstructure during densification process were observed.

Key words: Low temperature sintering, PZT, piezoelectric ceramics, piezoelectric properties, additives

1. INTRODUCTION

The low temperature sintering of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ has been studied by many researchers because of its advantages in suppressing or eliminating the volatilization of PbO in the sintering of conventional PZT ceramics which causes the composition fluctuation and the environmental pollution.¹⁾ Most attempts to lower the sintering temperature of PZT ceramics have been performed by employing single or complex low-melting oxides, carbonates, or fluoride additives directly.²⁻⁵⁾ However, the lowering of sintering temperature is normally accompanied by the sacrifice of electrical properties or the sintering temperature is still kept high. Thus it is very difficult to prepare low temperature sintered PZT ceramics with high piezoelectric properties.

$\text{Li}_2\text{CO}_3\text{-Bi}_2\text{O}_3$, CdO and $\text{Li}_2\text{CO}_3\text{-Bi}_2\text{O}_3\text{-CdCO}_3$ were used to reduce the sintering temperature of $\text{Pb}(\text{Zr,Ti})\text{O}_3$,⁶⁾ $\text{Pb}(\text{Zr,Ti})\text{O}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ⁵⁾ and Ba-doped $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics⁷⁾ respectively. In this study, the low temperature sintering of high performance $\text{PbZn}_{1/3}\text{Sb}_{2/3}\text{O}_3\text{-PbNi}_{1/2}\text{Te}_{1/2}\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PZS-PNS-PZT) ceramics (abbreviated as B-PZT, hereafter) was attempted by employing the

complex additives of $\text{Li}_2\text{CO}_3\text{-Bi}_2\text{O}_3\text{-CdCO}_3$ (abbreviated as LBC). The effects of the additives on the sintering temperature and the electromechanical properties were examined. The shrinkage behavior of the compacted body containing the complex additives was investigated.

2. EXPERIMENTAL

The B-PZT composition was prepared through a conventional mixed-oxide fabrication process. Commercially available oxides or carbonates were used as the starting materials. The powder mixtures of B-PZT composition was calcinated at 900°C for 3 hours, then mixed with the complex additives in alcohol. Discs specimen were formed at 800 kg/cm^2 in diameter of 22 mm and thickness of 2.5 mm and sintered at 980°C for different length of times.

Measurement of shrinkage of green bar was performed by using a Rigaku TAS-200 thermal mechanical analysis (TMA) at the heating rate 5°C/min . The isothermal shrinkage rate was detected at 980°C for 2h. A JEOL JSM-6320F scanning electron microscope (SEM) was used for the observation of morphology of the cross section of the sintered body

Piezoelectric and dielectric properties were measured by using an impedance analyzer (YHP-4194A) on the specimens polarized in silicone oil bath under 3kV/mm bias at 80°C for 10 min. Apparent density was determined by the Archimedes method.

3. RESULTS AND DISCUSSION

The LBC additives in various combinations were attempted to lower the sintering temperature of the B-PZT ceramics. The representative results are summarized in Table I, where K_p is electromechanical coupling factor, ϵ_r relative dielectric constant, Q_m mechanical quality factor, and $\tan \delta$ dissipation factor. The B-PZT ceramics is sintered at 1265°C for 1h. The B-PZT composition with 0.32mol% addition of LBC (abbreviated as B-PZT-C) were sintered at 980°C for 6h, where the additives LBC1: (0.08mol%Li₂CO₃-0.77mol%Bi₂O₃-0.15mol%CdCO₃), LBC2:(0.02mol%Li₂CO₃-0.11mol%Bi₂O₃-0.87mol%CdCO₃), LBC3: (0.38mol%Li₂CO₃-0.12mol%Bi₂O₃-0.50mol%CdCO₃). It can be found that the addition of LBC with the appropriate combination not only reduce the sintering temperature, but also improve the electromechanical properties of B-PZT ceramics. But if the combination of LBC is not chosen properly, its employment will affect or deteriorate the piezoelectric properties of B-PZT ceramics.

Table I. The electromechanical properties of the samples with and without LBC additives.

Sample	A	K_p (%)	ϵ_r	Q_m	$\tan \delta$	ρ (g/cm ³)
B-PZT		71.5	2966	58.9	1.73	7.76
B-PZT-C1	LBC1	45.3	1814	48.6	3.08	7.64
B-PZT-C2	LBC2	58.4	2572	58.4	2.08	7.76
B-PZT-C3	LBC3	71.9	3428	58.2	2.40	7.86

A: additives,

The shrinkage behavior of the compacted body containing LBC in different combinations reveals that the effect of the LBC additives on lowering the sintering temperature is relative to its composition (Fig.1). From Table I and Fig.1, LBC1, which is a complex additives with Bi₂O₃ as the main composition, can decrease the sintering temperature greatly, but

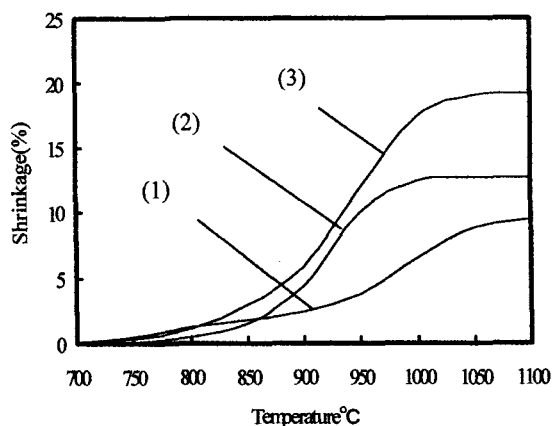


Fig.1.TMA curves of the samples.

(1) B-PZT-C1 (2) B-PZT-C2 (3) B-PZT-C3.

deteriorates the properties. LBC2 with CdCO₃ as a main composition can reduce the sintering temperature effectively, but affects the properties. LBC3 can work well on both aspects. So LBC3 is considered as the good additives for the purpose of this study.

Besides the composition of LBC additives, the sintering temperature of compacted body containing LBC also depends on the addition amount of the LBC additives. Fig.2 shows the relationship between the shrinkage behavior of the samples and addition amount of the additives LBC3. With the addition of more LBC3,

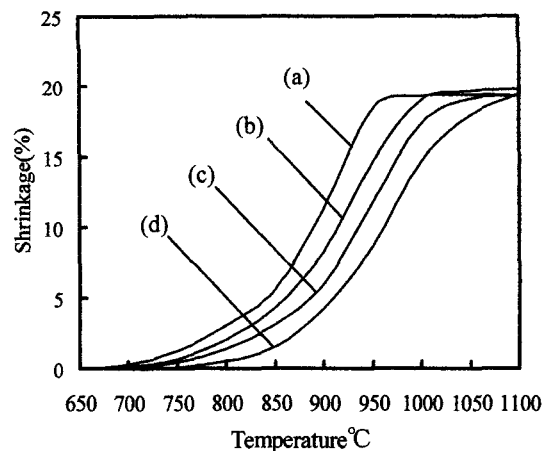


Fig.2. Thermal mechanical analysis (TMA) curves of the samples with (a) 1wt% LBC3 (b) 0.85wt% LBC3 (c) 0.70wt%LBC3 (d) 0.40wt%LBC3.

the sintering temperature becomes lower. In contrast to it, the change of the properties with the addition amount of LBC3 is different (Fig.3). The optimum properties are found at a certain addition amount.

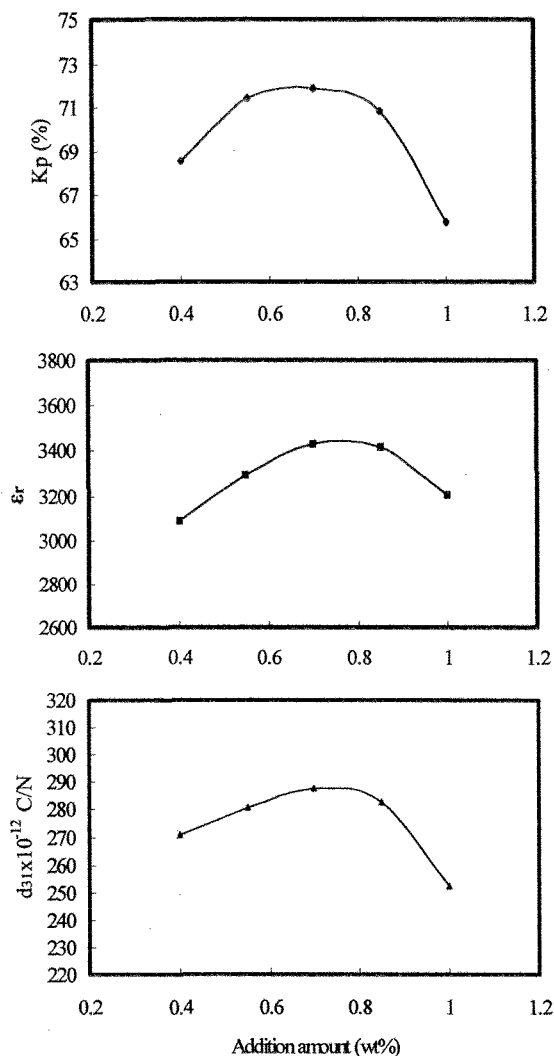


Fig.3. Variation of piezoelectric properties with LBC3 addition amount.

The isothermal shrinkage rate of samples B-PZT with LBC3 was measured (Fig.4). The result indicates that the densification process of the samples with LBC3 can be divided into three stages. According to Kingery model for the sintering in the presence of a liquid phase: $\Delta L/L \sim t^n$, where $n=1+y$ corresponds to rearrangement of particles and $n=0.33$ to a solution-precipitation process⁸⁾. The low temperature sintering of B-PZT-C3 seems to be consistent with Kingery model and characterized by a liquid phase sintering. The first stage with a slope of 1.20 is in agreement with the particles rearrangement. For the second stage with $n=0.38$, the samples are densified through a solution precipitation process. Last stage is considered to be the process of grain growth.

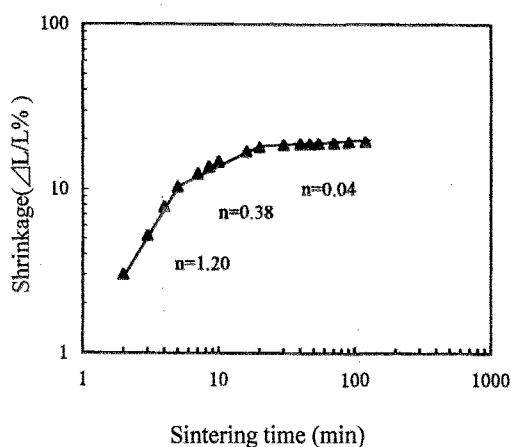


Fig. 4 Logarithm of linear shrinkage of B-PZT-C3 as a function of logarithm of sintering time at 980°C.

For the process of solution-diffusion precipitation, Kingery also gives that $\Delta L/L$ is proportional to $r^{-4/3}$ when t is constant, where r is initial particle size. The result shown in Fig.5 is fit to this relationship, which implies that the sintering rate is controlled by solution-diffusion precipitation through a liquid phase.

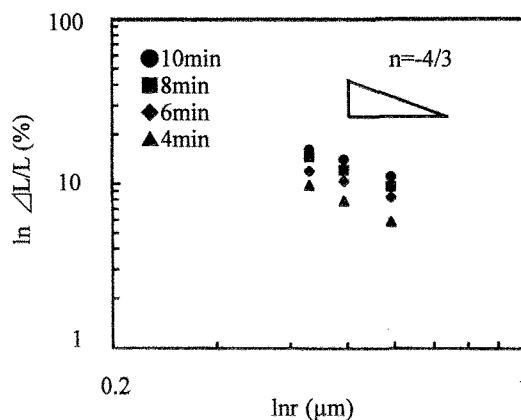


Fig.5 The shrinkage against the initial particle size.

The microstructure of the samples with the addition of LBC3 at 980°C for different time was observed (Fig.6), in which (a), (b), and (c) respectively correspond to three different sintering stages shown in Fig.4. In the initial stage of sintering, grains are rearranged in a way consistent with high density, but no grain growth was viewed. When sintering comes to second stage, the samples are more dense, meanwhile the grain growth takes place. With the further increase of time, the grains continue to grow and the grain

boundaries become clear. So the SEM observation also supports that the low temperature sintering of B-PZT with the additives LBC3 is a process of "liquid phase sintering"

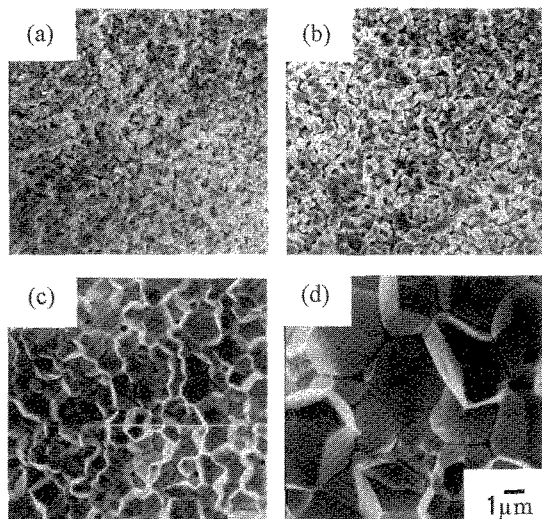


Fig.6. SEM micrographs of B-PZT-C3 sintered at 980°C for (a) 2 min, (b)10 min, (c) 30min, and (d) 6 h.

The DTA result of the samples with LBC3 indicates a liquid phase is formed at low temperatures (Fig.7), which is in agreement with the result from isothermal shrinkage kinetics. By means of the surface tension of the liquid, the densification process is accelerated greatly.

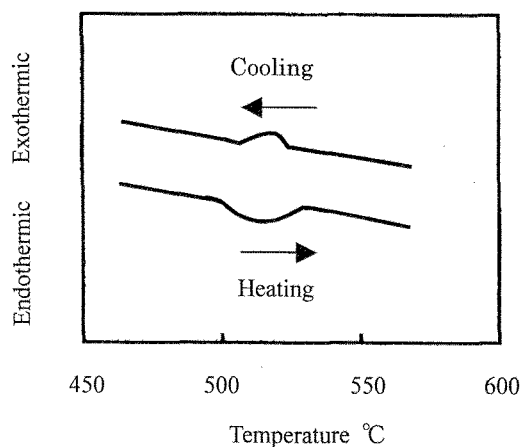


Fig.7. DTA curves of sample with LBC3 at heating and cooling rate of 5°C/min.

It should be mentioned that low temperature sintering of B-PZT ceramics with LBC3 additives is a complicate process. Although the densification characteristic of the samples with LBC3 is consistent

with Kingery model for sintering in the presence of a liquid phase, there still exists some difference in value of n . Such a difference suggests that beside effect of liquid phase on promoting the densification, the chemical activities of Li_2CO_3 and CdCO_3 in LBC would probably be contributive to enhance the densification rate of the sample with LBC3 additives by activating the grain surface of B-PZT composite.

4. CONCLUSION

The low temperature sintering of PZS-PNT-PZT ceramics was achieved by employing a slight amount of proper complex additives Li_2CO_3 - Bi_2O_3 - CdCO_3 as a sintering aid, with an improvement on the piezoelectric properties. The sintering process is characterized by a liquid phase sintering. The sintering rate is controlled by solution-diffusion precipitation. The formation of liquid phase at low temperature is a main reason why the densification of compacted bodies is enhanced remarkably.

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