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Low-Firing Pb(Zr,Ti)O₃-Based Multilayer Ceramic Actuators Using Ag Inner Electrode

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We investigated the low firing of Li_2CO_3 added $0.2Pb(Mg_{1/3}Nb_{2/3})O_3$ - $0.3Pb(Fe_{1/2}Nb_{1/2})$ - $0.5Pb(Zr_{0.475}Ti_{0.525})O_3$ (PMN-PFN-PZT) ceramics and multilayer actuators (MLAs) using Ag inner electrodes. It was found that 0.1 wt% Li_2CO_3 was quite effective in lowering the sintering temperature of PMN-PFN-PZT ceramics from 1,100℃ down to 900℃ without deteriorating their piezoelectric ceramics (d_{33} = 425 pC/N and k_p = 61.9%). However, excess Li_2CO_3 up to 0.3 wt% brings about unwanted problems such as the formation of a $LiPbO_2$ secondary phase and subsequent degradation in the piezoelectric properties. Using 0.1 wt% Li_2CO_3 added PMN-PFN-PZT ceramics, MLAs with Ag inner electrodes were successfully fabricated, resulting in a normalized strain of 580 pm/V at an electric field of 1.5 kV/mm.

Keywords: Piezoelectric ceramics, Multilayer actuator, Internal electrode, Low firing

1. INTRODUCTION

Piezoelectric and electrostrictive actuators are widely used in applications requiring precision displacement control or high generative force (i.e., optical stage, precision mechatronic systems, and semiconductor devices) [1,2]. In particular, multilayer actuators (MLAs) using Pb(Zr,Ti)O₃ (PZT) ceramics have attracted much attention because of their merits, such as rapid operation, low power consumption, high precision control, and little noise [3,4] compared with conventional electromagnetic actuators.

Currently, most MLAs adopt expensive AgPd alloys as internal electrodes because they are stable between piezoelectric ceramic layers throughout a high-temperature sintering process. Therefore, there is ample necessity to explore inexpensive conducting materials as an internal electrode for low-cost and low-

firing MLAs. For utilization of Ag as an inner electrode, co-firing temperature should be lower than the melting point of Ag, which makes it difficult to attain excellent piezoelectric properties, since they are generally improved with microstructural evolution. To overcome such problems, the low-temperature sintering of PZT ceramics has been attempted by a variety of approaches: sol-gel method [5], reactive sintering [6], fine powders prepared by high-energy ball-milling [7,8], and low-melting sintering aids, such as Li_2O [9], $LiBiO_2$ [10], $LiSbO_3$ [11], Li_2CO_3 [12], and CuO [13,14].

In contrast, piezoelectric ceramics should possess high electric field-induced strain (EFIS) properties if they are to be applied to MLAs. It was reported that $Pb(Mg_{1/3}Nb_{2/3})O_3$-Pb(Zr,Ti) O_3 (PMN-PZT) ceramics exhibit high piezoelectric constants as well as EFIS near the morphotropic phase boundary [14-17]. Moreover, our recent study on $Pb(Fe_{1/2}Nb_{1/2})$ added PMN-PZT complex perovskite ceramics demonstrated enhancement in their dielectric and pyroelectric properties by adding Li_2CO_3 as a sintering aid [15]. Therefore, this study investigates the effects of Li_2CO_3 on the sintering behavior and piezoelectric properties of $0.2Pb(Mg_{1/3}Nb_{2/3})O_3$ - $0.5Pb(Zr_{0.475}Ti_{0.525})O_3$ - $0.3Pb(Fe_{1/2}Nb_{1/2})$ (hereinafter, PMN-PFN-PZT) ceramics and the possibility of

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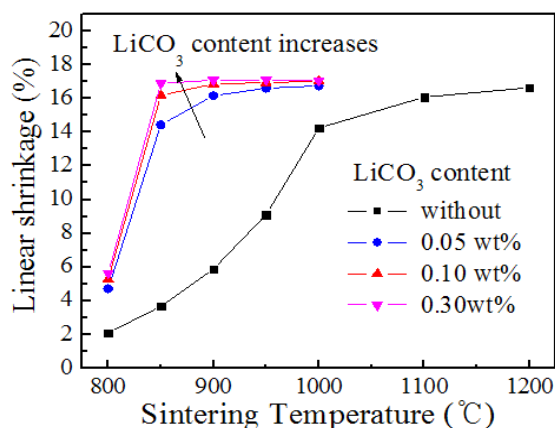
Fig. 1. Effect of Li$_2$CO$_3$ addition on the firing shrinkage of PMN-PFN-PZT ceramics.

Fig. 2. Surface micrographs of PMN-PFN-PZT ceramics sintered at 900℃ for 2 hours; (a) without, (b) 0.05 wt%, (c) 0.1 wt%, (d) 0.3 wt% Li$_2$CO$_3$ added specimens.

their application to low-firing MLAs using Ag inner electrodes.

2. EXPERIMENTS

Ceramic powder, with a composition of PMN-PFN-PZT, was synthesized using the columbite precursor method, which consists of a two-stage calcination process. In the first step, a mixture of MgO, Fe$_2$O$_3$, Nb$_2$O$_5$, ZrO$_2$, and TiO$_2$ powders (99.5% purity; Cerac Specialty Inorganics, Milwaukee, WI, USA) was properly weighed, according to the formula, and ball-milled with zirconia balls and deionized water for 24 hours. The mixed powders were dried and then calcined at 1,100℃ for 2 hours, to form a columbite phase of (Mg,Fe)Nb$_2$(Zr,Ti)O$_6$. In the second step, a stoichiometric amount of PbO, with 99.5% purity, (supplied by the same company) was added and mixed with calcined powders by ball-milling for 24 hours again. After drying, it was re-calcined at 850℃ for 2 hours. Before milling the calcined powders, Li$_2$CO$_3$ was added as a sintering aid in the range of 0.05 to 0.3 wt%. Ceramic pellets with a 12-mm diameter were prepared by dry pressing at 98 MPa and fired at temperatures between 800℃ and 200℃ for 2 hours, in air.

MLAs were prepared using 0.1 wt% Li$_2$CO$_3$ added PMN-PFN-PZT powders and thick film Ag. Piezoelectric ceramic sheets were obtained by tape casting ceramic slurry containing a mixture of piezoelectric powders, organic binders, a plasticizer, and solvents. The green sheets were cut into 10 × 10 cm^2 using a knife cutting machine. Ag paste was screen-printed on the ceramic sheet, and then laminated with 12-layers of ceramic sheets. After cutting into 10 (W) × 15 (L) mm^2, the samples were soaked at 500℃ for 6 hours, in air, to remove organic additives, and then co-fired at 850-950℃ for 5 hours, in air.

3. RESULTS AND DISCUSSION

Figure 1 shows the firing shrinkage of PMN-PFN-PZT ceramics as a function of sintering temperature (T_s) and the amount of Li$_2$CO$_3$ sintering aid. Without Li$_2$CO$_3$ addition, it is seen that sufficient densification occurs at temperatures higher than 1,100℃, while Li$_2$CO$_3$ added specimens exhibit densification at a temperature as low as 900℃, indicating that Li$_2$CO$_3$ is quite useful to lower T_s by at least 200℃, similarly to previous reports on Li$_2$CO$_3$ added PMN-PZT ceramics [12,15].

The effect of Li$_2$CO$_3$ on the sintering behavior is more clearly understood from microstructural observation. Figure 2 displays

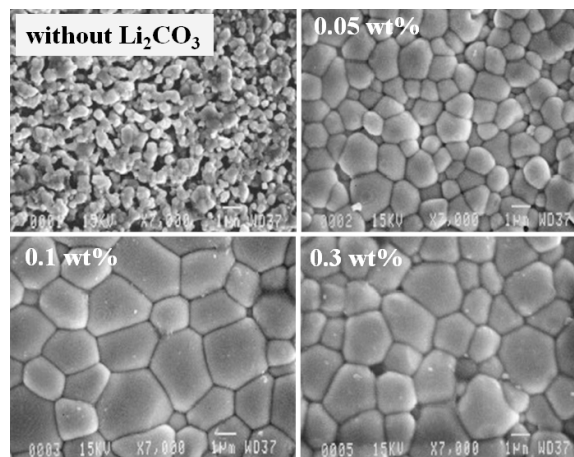the surface micrographs of specimens sintered at 900℃ for 2 hours. As seen in Fig. 2(a), a specimen sintered without L$_2$CO$_3$ reveals little grain growth and densification because the particle size is almost similar to that of a green compact (~0.5 μm), and many pores can be also observed. However, Li$_2$CO$_3$ added specimens show dense microstructures and significant grain growth; the average grain size for 0.05, 0.1, and 0.3 wt% Li$_2$CO$_3$ is 1.4, 2.2, and 1.8 μm, respectively.

Such an enhancement in density and grain size by Li$_2$CO$_3$ was also observed in our previous work on PMN-PZT ceramics with added Li$_2$CO$_3$ [7] or Li$_2$O [9]. A possible explanation is that sintering is enhanced by formation of a transient liquid phase at the initial stage [16], which is in turn dissolved into a matrix at a later stage of sintering. In this work, a low-melting Li compound was also detected from X-ray diffraction (XRD) analysis at high Li$_2$CO$_3$ levels, as shown in Fig. 3, which compares XRD reflections of specimens for different Li$_2$CO$_3$ amounts. All specimens correspond to perovskite symmetry, while a secondary phase that is identified as LiPbO$_2$ is observed when the amount of Li$_2$CO$_3$ reaches 0.3 wt%.

Figure 4 presents the piezoelectric constant d_{33} and planar piezoelectric coupling coefficient of PMN-PFN-PZT ceramics as a function of Li$_2$CO$_3$ content. Both d_{33} and k_p reach their highest levels when Li$_2$CO$_3$ content goes to 0.1 wt%, whose values are 425 pC/N and 61.9%, respectively. Further addition of Li$_2$CO$_3$ results in drops in both d_{33} and k_p, which is believed to be due to the combined effects of decreased grain size, as seen in Fig. 2, and the secondary phase that was identified by XRD in Fig. 3. It should also be noted that the grain-size dependence of the piezoelectric constants in this work is very similar to a report by Swartz [17]. This phenomenon might be attributed to the inhibition of domain wall movement by grain boundaries whose effect becomes stronger as the grain size decreases.

MLAs were fabricated by laminating PMN-PFN-PZT green sheets with a screen-printed Ag-ceramic electrode. After co-firing, the dimension of a MLA was about 8 (W) × 12 (L) × 1 (T) mm^3, in which 12 ceramic and 11 Ag inner electrode layers are alternatively stacked. The fractured surface of specimens sintered at 850, 900, and 950℃ was observed using a scanning electron microscope and the results are provided in Fig. 5. Low-magnification micrographs (left column of Fig. 5) show well laminated multilayers with clear interfaces and a uniform thickness of about 80 μm in piezoelectric layers.

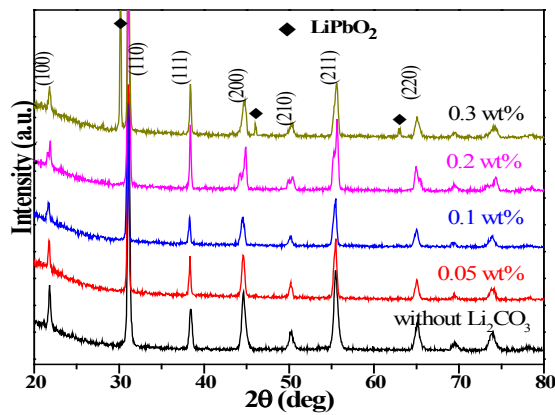In the case of inner electrode layers, the morphologies are

Trans. Electr. Electron. Mater. 12(6) 249 (2011): H.-S. Han *et al.*

251

Fig. 3. X-ray diffraction patterns of PMN-PFN-PZT ceramics sintered with different amounts of Li$_2$CO$_3$ sintering aid.

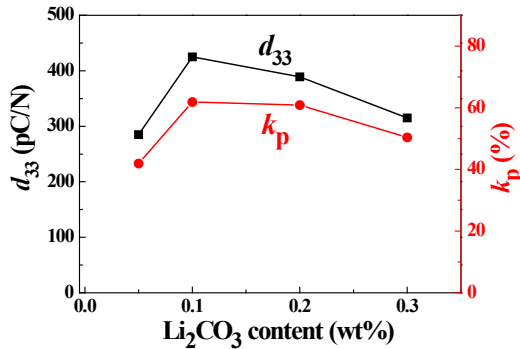
Fig. 4. The piezoelectric coefficient (d_{33}) and planar piezoelectric coupling coefficient (k_p) of PMN-PFN-PZT ceramics as a function of Li$_2$CO$_3$ content.
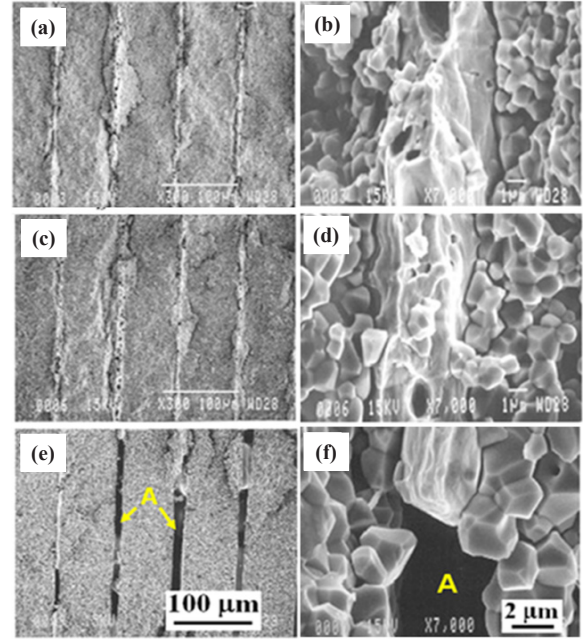

Fig. 5. The fractured cross-sectional micrographs of 0.1 wt% Li$_2$CO$_3$ added PMN-PFN-PZT/Ag MLAs co-fired at different temperatures for 5 hours. The sintering temperature was 850℃ for (a) and (b), 900℃ for (c) and (d), and 950℃ for (e) and (f), respectively.
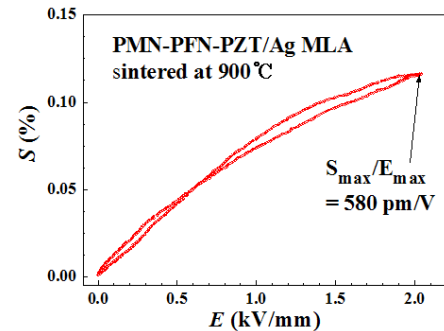

Fig. 6. Unipolar strain versus electric-field (*S-E*) hysteresis loop of 0.1 wt% Li$_2$CO$_3$ added PMN-PFN-PZT/Ag MLAs co-fired at 900℃ for 5 hours.

more clearly seen in higher-magnification micrographs (right column). The Ag thickness is not uniform in a range of 3-5 μm, moreover, their connectivity is broken when $T_s = 950$℃, as indicated by arrows (region A), which seems to be due to the viscous flow of Ag near its melting point of about 962℃ [18]. It was also reported that Ag thick films become unstable at 950℃ in the case of the PMN-PZT/Ag multilayers [19].

EFIS was measured for a MLA sintered at 900℃, and the result is displayed in Fig. 6. The normalized strain S_{max}/E_{max} was measured as 580 pm/V, which is higher than the small signal d_{33} of 425 pC/N characterized with a Berlincourt d_{33} meter, as seen in Fig. 4, and is promising for high strain actuator applications. The difference between d_{33} and S_{max}/E_{max} indicates that piezoelectric constant obtained from the piezoelectric effect is different from that measured from the converse piezoelectric effect. Such a difference seems to be larger in lead-free piezoelectrics [20,21] than in Pb-based ones, even though exact understanding is still lacking.

4. CONCLUSIONS

The effects of Li$_2$CO$_3$ on the sintering behavior and piezoelectric properties of PMN-PFN-PZT ceramics have been investigated. It was found that Li$_2$CO$_3$ is quite effective in lowering T_s from 1,100℃ down to 900℃ in PMN-PFN-PZT ceramics without degradation of their piezoelectric ceramics. However, excess Li$_2$CO$_3$ up to 0.3 wt% brings about problems, such as the formation of an unwanted Li$_2$PbO$_3$ secondary phase and subsequent degradation in the piezoelectric properties. Using 0.1 wt% Li$_2$CO$_3$ added PMN-PFN-PZT ceramics, MLAs using Ag inner electrodes were successfully fabricated, resulting in a normalized strain of 580 pm/V at a dc field of 1.5 kV/mm. This result is very promising for low-cost MLAs.

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252

Trans. Electr. Electron. Mater. 12(6) 249 (2011): H.-S. Han *et al.*

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