Effect of Yb Addition on the Sintering Behavior and High Power Piezoelectric Properties of Pb(Zr,Ti)O$_3$-Pb(Mn,Nb)O$_3$

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Abstract

0.9Pb(Zr$_{0.61}$Ti$_{0.39}$)-0.1Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$ piezoelectric ceramics doped with Yb$_2$O$_3$ were prepared by conventional ceramic processing, and the effects of the Yb doping on the sintering behavior and high power piezoelectric properties were investigated. XRD measurements indicated that the piezoelectric ceramics with Yb$_2$O$_3$ in this study were a single phase of polycrystalline perovskite. The sintering density was strongly affected by small amount of Yb$_2$O$_3$ addition. Vibration velocity, which is one of the most important factors for high power piezoelectric applications, as high as 1.0 m/s (rms value), was obtained from the 0.2 mol% Yb$_2$O$_3$ doped sample. This value is about 2.5 times higher than that for commercialized hard PZT ceramics.

I. Introduction

High power piezoelectric ceramics are applied to various devices, such as ultrasonic motors and piezoelectric transformers, as materials which can convert electrical energy to mechanical energy or vice versa at the electromechanical resonance. For these applications, piezoelectric ceramics exhibiting a high vibration velocity are used. Because the vibration velocity is represented in proportion to the product of electromechanical coupling factor k and mechanical quality factor Q$_m$, materials with a large electromechanical coupling factor and a large mechanical quality factor are used. The best examples of such high power piezoelectric ceramics are compositions comprising of PbZrO$_3$-PbTiO$_3$-Pb(Sb$_{1/3}$Mn$_{2/3}$)O$_3$ (PZT-PSM)[1-3] and PbZrO$_3$-PbTiO$_3$-Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZT-PMnN).[4]

Ise *et al*. reported the high power characteristics of PZT-PMnN piezoelectric system. This system showed very high vibration velocity compare to hard PZT and commercial PZT-PSM system.[4] Recently, Gao *et al*. reported the combinatory effect of rare earth element doping on the piezoelectric properties of PZT-PSM system.[1] By doping rare earth element such as Yb^{+3} or Eu^{+3}, electromechanical coupling factor k (softening effect) and mechanical quality factor Q$_m$ (hardening effect), both were improved. Therefore the longitudinal vibration velocity of the samples was dramatically improved.

In this study, the effect of Yb$_2$O$_3$ addition on the sintering behavior and the high power piezoelectric characteristics (especially vibration velocity) of PZT-PMnN system are described. It is expected that the combinatory 'hard' and 'soft' piezoelectric characteristics can be introduced for this system when rare earth elements are doped as in the previous studies. Accordingly, very high vibration velocity is expected from this system, because the vibration velocity of piezoelectric element is strongly related with electromechanical coupling factor and mechanical quality factor.

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II. Experimental Procedure

Conventional ceramic processing by using reagent grade oxide powders was conducted to prepare the samples. Pellets (12.7 × 3 mm) and rectangular bars (15 × 50 × 3 mm) were fabricated. Pressureless sintering of the ceramics is performed in a high purity alumina crucible at 1000 to 1200 ^{o}C for 2 hours. Apparent sintered densities were measured by the Archimedes method with Xylene (ρ= 0.861 g/cm^3 at 20 ^{o}C). Dielectric properties were obtained by measuring the capacitance and loss using an LCR meter (HP model 4284). To determine T_c, capacitance measurements were made as a function of temperature in an automated temperature controlled furnace interfaced with a computer for data acquisition. The piezoelectric coefficient d_{33} was recorded from one-day aged samples using a Berlincourt-d33 meter (IAAS ZJ-2, Beijing, China). The electromechanical coupling factor k_p and mechanical quality factor Q_m were measured using an impedance analyzer (Model HP 4194) based on the IEEE standards. The vibration velocity υ_o was measured using laser doppler vibrometers (LDV) Model OFV-3001 and OFV-511 (Polytec PI). The 4-pt flexural strength (σ_f) was measured with an universal testing machine (AG-500E, Shimadzu Co., Japan). Fracture toughness (K_{IC}) was determined with the IS (indentation strength) method using Vickers hardness tester (DVK-2S, Matsuzawa Co., Ltd., Japan) and universal testing machine.

III. Results and discussion

Figure 1 shows the XRD patterns of PZT-PMnN ceramics with several Yb$_2$O$_3$ contents of 0 (a), 0.2 (b), 0.5 (c), and 1.0 (d) mol%. All the peaks are assigned to rhombohedral perovskite structure. This indicates that the ceramics with Yb$_2$O$_3$ shown above are a single phase of polycrystalline PZT-PMnN perovskite.

Figure 2 shows apparent sintered density as a function of sintering temperature for PZT-PMnN ceramics with several Yb$_2$O$_3$ contents. All samples were sintered for 2 hours at each temperature. With increasing sintering temperature, the density is increased gradually. For the samples with 0.2 and 0.5 mol% Yb$_2$O$_3$, the density is saturated and fully dense at around 1100 ^{o}C. While this ceramics are expected to be especially useful in multilayered transformers, sintering temperature of 1100 ^{o}C would be preferred for multilayer designs because of relatively low cost metals, such as low Pd-fraction Ag-Pd alloys, could be employed for the internal electrodes.[5]
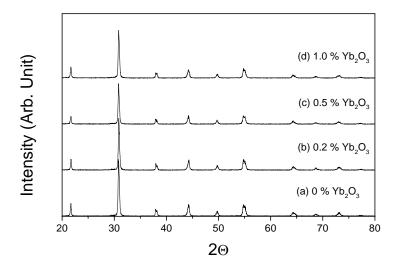

Fig. 1. XRD patterns of PZT-PMnN sintered body with Yb$_2$O$_3$ content of (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 mol%. All samples are sintered at 1200 ^{o}C for 2 h.
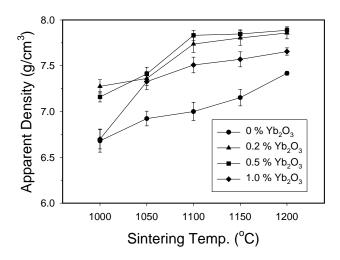
Fig. 2. Apparent density as a function of sintering temperature.

The fracture surfaces of samples sintered at 1200 ^{o}C for 2 hours were examined by SEM and showed in Fig. 3. The doping of Yb$_2$O$_3$ has significant influences on the microstructure of PZT-PMnN ceramics. When pure PZT-PMnN was heated to 1200°C for 2 hours, it shows liquid phase on the microstructure. Contrary to this, the microstructures of doped with Yb$_2$O$_3$ are quite different from that of pure PZT-PMnN. When the Yb$_2$O$_3$ added compositions were sintered at the same condition, liquid phase was not existing and it seems to be perfect solid state sintered microstructure. And the sinterability of the composite is improved as illustrated in Fig. 2. When Yb$_2$O$_3$ is added to PZT-PMnN as a solid solution, point defects might be created, and the created point defect might be the reason of the suppression of liquid phase during sintering.

Figure 4 shows the temperature dependence of the dielectric constant and loss at 1 kHz. The room temperature dielectric constant and loss were almost constant with changing Yb$_2$O$_3$ doping content. The temperature of the dielectric constant maximum (Curie Temperature, T$_c$), which is the effective phase transition temperature, is not changed either and the values were in the range of 305 ~ 310 ^{o}C, which is high enough for high power piezoelectric applications such as piezo-transformers and piezoelectric ultrasonic motors. The Curie temperature is one of important properties for high power piezoelectric applications. During high power operation, generated heat may cause the de-polarization of the piezoelectric. If the Curie temperature of the piezoelectric materials is not high enough, performance of piezoelectric devices can be dramatically degraded because of de-poling and temperature dependence of piezoelectric properties.

Piezoelectric properties and mechanical properties are summarized in table 1. The piezoelectric proerties are obtained from impedence curve under driving voltage of 0.5 V$_{p-p}$. As the amount of Yb$_2$O$_3$ dopant increased from 0 to 0.5 mol%, electromechanical coupling factor (k$_p$) increased by 17%, and the absolute value of piezoelectric constant (d$_{33}$) decreased from 110 to 105 pC/N, however, the change of d$_{33}$ is negligible.

Table 1 also shows that the mechanical quality factor (Q$_m$) of Yb$_2$O$_3$ added PZT-PMnN decreased from 2200 to 540 as the amount of Yb$_2$O$_3$ addition increased from 0 to 1.0 mol%.

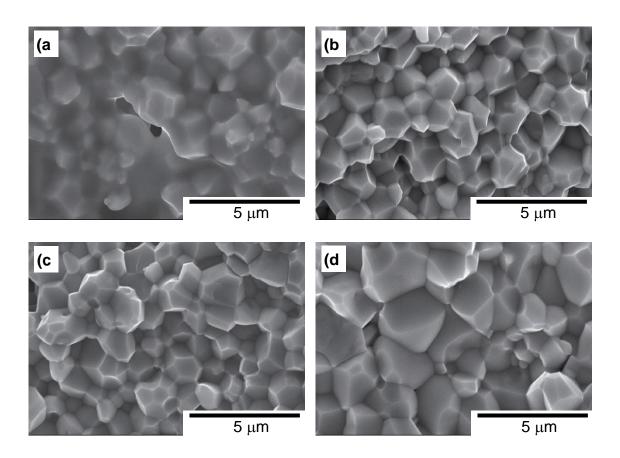Fig. 3. SEM micrographs of fracture surfaces of sintered body. (a) 0, (b) 0.2, (c) 0.5, and (d) 1.0 mol% Yb_2O_3 doped sample sintered at 1200^oC for 2 hours
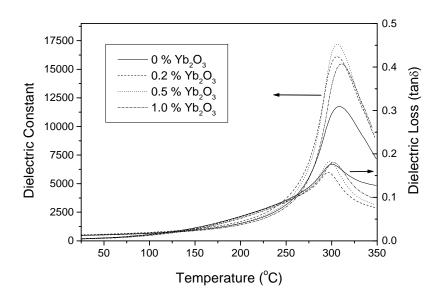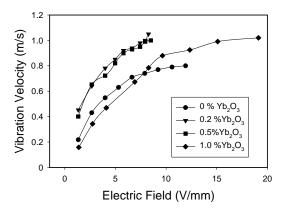

Fig. 4. (a) Dielectric constant and (b) dielectric loss as function of temperature for PZT-PMnN with various Yb_2O_3 doping concentrations. All samples were sintered at 1200 ^oC for 2 hours.

Table 1. Dielectric and piezoelectric properties of PZT-PMnN with changing Yb_2O_3 doping content. Samples are sintered at 1200 ^{o}C for 2 hours.

Yb_2O_3 (mol%)	Density (g/cm^3)	T_c (^{o}C)	k_p	$\varepsilon_3^T/\varepsilon_o$	tan δ	d_{33} (pC/N)	Q_m	V_{max} (m/s)	σ_f (MPa)	K_{IC} (MPam$^{1/2}$)
0.0	7.55	309	0.333	350	0.014	110	2200	0.79	84±5	1.23±0.12
0.2	7.85	306	0.382	365	0.023	108	1100	1.00	121±6	1.43±0.16
0.5	7.85	306	0.389	340	0.007	105	850	0.96	114±5	1.38±0.18
1.0	7.63	310	0.355	330	0.007	104	540	0.95	94±7	1.33±0.13

For practical piezoelectric devices, mechanical properties such as fracture strength (σ_f) and fracture toughness (K_{IC}) are important in the viewpoint of reliability.   The samples with Yb_2O_3 addition, the mechanical properties are higher than those of undoped samples.   The superior mechanical properties of 0.2 and 0.5 mol% Yb_2O_3 doped samples are mainly due to higher density and finer grain size. Since the fracture mode of specimens is intergranular fracture, the lower content of liquid phase (or solid state sintering) of the specimen with Y_2O_3 can be the other reason of superior mechanical properties.

Figures 5 and 6 show vibration velocity (υ_o, rms value) as a function of the electric field (E_{ac}, rms value) and temperature rise as a function of vibration velocity of the samples, respectively. With increasing E_{ac}, saturation in the value of υ_o started and the value was higher than 0.95 m/s for the Yb_2O_3 added samples.

Fig. 5. Vibration velocity (u_o) as a function of applied electric field (E_{ac}).

Fig. 6. Temperature rise as a function of vibration velocity.

This saturation was due to a decrease in mechanical quality factor Q_m with increasing E_{ac} above a critical vibrational level, as well as heat generation. The vibration velocity is related with the piezoelectric constant (d), permittivity (ε), elastic compliance (s), electro-mechanical coupling factor (k), and mechanical quality factor (Q_m).[6] Since the piezoelectric properties shown in table 1 were obtained under very low electric field (< 0.2 V/mm), the vibration velocity in the fig. 5 is not directly proportional to those piezoelectric properties. Therefore the samples with 0 and 1 mol% Yb_2O_3 could show lower vibration velocity at the electric field of 1-2 V/mm, even there is no temperature rise (fig. 6). It is well known that high Q_m

values can be dramatically decreased above certain critical high electric field driving level (or vibration velocity).[6,7] The mechanical quality factor of the sample with 0 mol% Yb_2O_3 might be changed significantly at the electric field level of 1-2 V/mm. At $E_{ac} \sim 8.5$ V/mm (rms value), υ_o was found to be as high as 1.0 m/s (rms value) for a sample with 0.2 and 0.5 mol% Yb_2O_3 doped samples. These high vibration velocity values are around 2.5 times higher than that of the conventional hard PZT ceramic which had a value of around 0.40 m/s (rms value) at the higher E_{ac} drive level.[6] The maximum vibrational velocity, υ_{max} (at temperature rise $\Delta T = 20°C$), for 0.2 mol% Yb_2O_3 doped sample was found to be 1.0 m/s, which is higher than that of PZT-PSM with Yb or Er doped composition which shows very high vibration velocity, reported by Gao et al.[1] and other high vibration velocity piezoelectric materials. It is expected that this exceptionally high vibration velocity can generate more power and covert electric energy. PZT-PMnN-Yb_2O_3 piezoelectric materials can be utilized for high power piezoelectric devices such as piezoelectric transformers and ultrasonic motors.

IV.   Conclusion

The dielectric and piezoelectric characteristics were investigated for the $0.9Pb(Zr_{0.61}Ti_{0.39})-0.1Pb(Mn_{1/3}Nb_{2/3})O_3 - xYb_2O_3$ system ($0 < x < 0.01$). Addition of Yb_2O_3 was effective for improving high power piezoelectric characteristics such as vibration velocity of PZT-PMnN system. Curie temperature was high enough and did not changed with Yb_2O_3 doping and the value was around 310 ^oC. High vibration velocity (υ_o) were improved from 0.79 m/s to 1.0 m/s by doping of 0.2 mol% Yb_2O_3. This value is exceptionally higher than commercial hard PZT piezoelectric ceramics. The mechanical strength and fracture toughness of Yb_2O_3 doped sampes higher than those of undoped sampes and the values were 121 MPa and 1.43 $MPam^{1/2}$. It is expected that this piezoelectric material can be utilized for high power piezoelectric devices such as piezoelectric transformers and ultrasonic motors.

Acknowledgement

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