Electric properties of low-temperature sintering Zn-doped PZT based ceramics and characterizations on applied SAW devices

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Abstract: To develop the ceramic sheet with low sintering temperature for Surface Acoustic Wave (SAW) devices applications, the low cost and feasible material systems with moderate piezoelectric properties, good dielectric properties, higher Curie temperature and higher effective energy transformation ratio for devices would be explored. The piezoelectric ceramics with compositions of $PbCa_{0.01}[(Mn_{1/3}Nb_{2/3})_{0.06}-(Zr_{0.48}Ti_{0.52})_{0.94}]O_3$ (PMnN-PZT) + 0.1 wt.% CuO + x wt.% ZnO (abbreviated PMNZTC-Z10x) had been prepared by the conventional mixed-oxide method. The ZnO dopants were used as the sintering aids to improve the bulk density and lower the sintering temperature. The phase structurse, microstructures, dielectric and piezoelectric properties, and ferroelectric properties versus ZnO additives were systematically investigated. Experimental results showed that the sintering temperature could be lowered down to 980 °C and still keep reasonably good characteristics. We found that the addition of co-doping of ZnO could enhance the relative dielectric constant, coupling factors, and remnant polarization compared to those of undoped PMnN-PZT ceramics.

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1. Introduction

Piezoelectric lead zirconate titanate (PZT) with the perovskite structure (general formula ABO_3) have been extensively used as sensors, actuators, and transducers due to their high electromechanical properties at the morphotropic phase boundary (MPB) region [1,2]. To fit the mentioned device applications, many aliovalent additions of PZT network system occupying the A-site or B-site of crystal structure induce the “soft” or/and “hard” effect to improve the piezoelectric activity and decrease the internal loss to minimize the energy dissipation during electromechanical transformation. The ternary PMnN-PZT based material systems can meet the above requirements and have good properties on actuators and transducers. Up to now, lead-free piezoelectric material systems have been developed to prevent from PbO volatilization leading to environmental pollution. However, they are difficult to be fabricated at low temperature sintering below 1000 °C possessing high dielectric constant, high electromechanical coupling factor using the conventional solid-state method Therefore, the concern about the development of low-temperature sintered PZT based piezoelectric material is getting important issue. In the past, CuO had been used as an additive to lower the sintering temperature of ceramics [3, 4]. While Ahn et al. showed the ZnO was effective in improving the piezoelectric properties [5]. And M. S. Yoon showed that ZnO could enhance the piezoelectric voltage output coefficient and piezoelectric charge constant [6]. In this study, we systematically investigated the doping effects on the dielectric, piezoelectric, ferroelectric properties by introducing ZnO dopants into the modified PMnN-PZT ceramics via different sintering temperature to meet the requirements in the fields of the acoustic sensor devices.

In addition, we used this developed low temperature sintered PMnN-PZT composition as the anisotropic ceramics substrate to fabricate the SAW devices and their properties were investigated.

2. Experimental Procedure

The compositions chosen in the present study were $PbCa0.01[(Mn_{1/3}Nb_{2/3})_{0.06}-(Zr0._{48}Ti_{0.52})_{0.94}]O_3$ (PMnN-PZT) + 0.1 wt.% CuO + x wt.% ZnO (abbreviated PMNZTC-Z10x) by conventional mixed-oxide method. The powders were calcined at 880 °C for 3 h. Thereafter, ZnO were added to the calcined powders, and then were ball-milled for 24 h and dried again, and then granulated. The samples were pressed into disc shape and sintered at 980-1050 °C for 4h in a covered alumina crucible. The sintered samples were polished and were screen-printed with silver paste on both opposite faces, followed by firing 820 °C for 10 minutes. Then, the electroded samples were poled at a

DC electric field of 3kV/mm for 30 min. in a 150 °C silicon oil bath. The physical properties were measured by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and calculated by Archimedes method. The dielectric, ferroelectric, and piezoelectric properties were measured by Agilent 4294A impedance analyzer according to IEEE standards. The SAW properties of velocity (V_p) and the effective coupling factor (k^2) were obtained by network analyzer HP8714ES from the equation in reference [7].

3. Results and Discussion

The bulk densities of ZnO doped samples presenting the maximum values are between 7.82 g/cm^3 and 7.85 g/cm^3. And the preferred sintering temperature of PMnN-PZT specimens with ZnO doped PMNZT-C should be of 980-1020 °C. The SEM micrographs of ZnO doped PMNZT-C specimens versus the amount of ZnO additive, sintered at temperature 980 °C, can be observed that the microstructures of ZnO-added PMNZT-C are much denser, and present slightly grain growth with increasing the ZnO content, then drop as x > 2. In XRD patterns, no obvious second phase ($Pb_3Nb_4O_{13}$) can be detected, but the crystal structures of the samples are modified a little by the addition of ZnO content. It can be concluded that Zn ionexit mainly in the state of Zn^{2+} which enters into the perovskite structure of BO_6 octahedron to substitute for the B-site ion resulting in the structure deformation, and vacancies are created.

The dielectric constant and dielectric loss for PMNZTC-Z10x specimens as a function of the amount of ZnO versus temperature were measured at frequency of 100 KHz as shown in Fig.1.

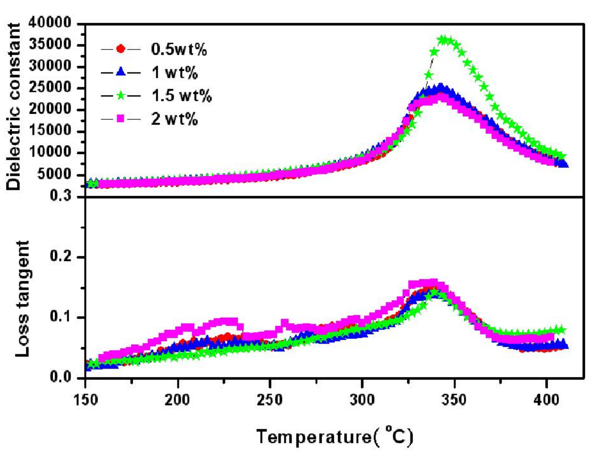

Fig.1 The dielectric constant and loss tangent as a function of the ZnO amount versus temperature

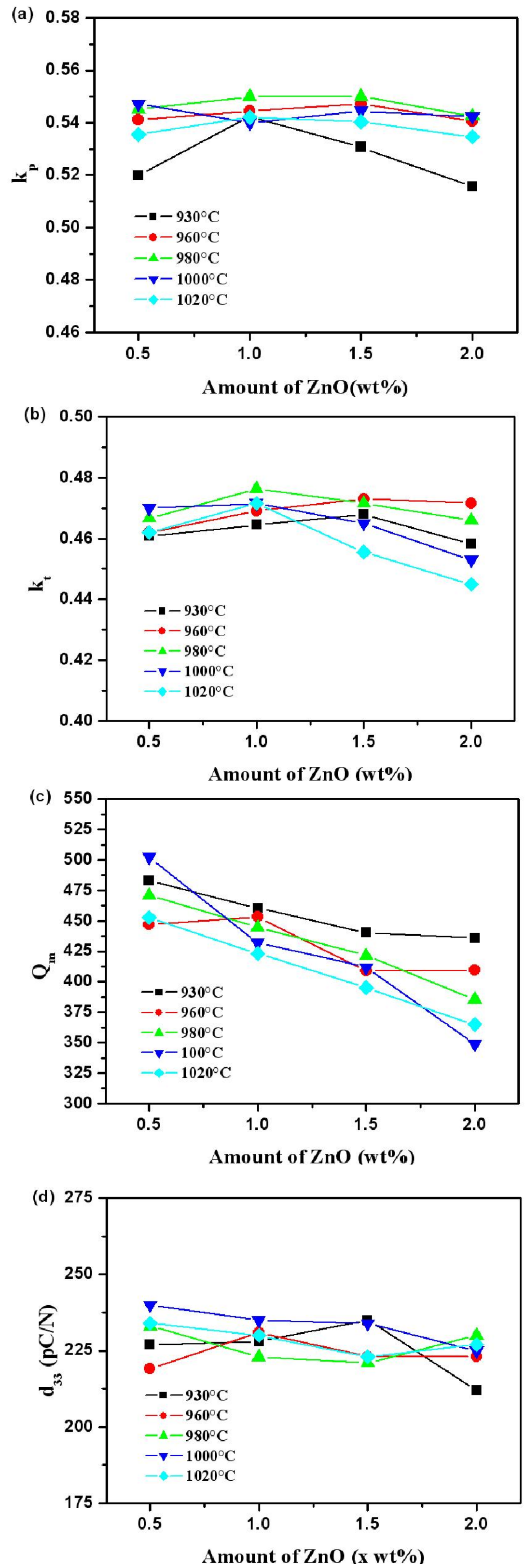

Fig. 2 The piezoelectric properties: (a) K_p, (b)K_t, (c) Q_m and (d) d_{33}

The Curie peak is increased with increasing the amount of ZnO additive and the maximum curie peak occurs at x=1.5. The dielectric constant increases with increasing ZnO, then decreased in dielectric constant as x > 2. Meanwhile, the dielectric loss decreased with ZnO content decrease. It can be interpreted that the dielectric constant increases due to the increase of grain size as increasing the amount of ZnO additive leading to polarizability increased and make domain wall motion shift easily resulting in dielectric constant increase [8].

In addition, from the Fig. 1 and 2 the optimum specimens, x=1, presented the value of electromechanical coupling factor (k_p) (k_t), mechanical quality factor (Q_m), piezoelectric charge constant (d_{33}), dielectric constant ($\varepsilon_{33}^T/\varepsilon_0$), loss tangent (tanδ), coercive field (E_c), remanent polarization (P_r), temperature coefficient of resonant frequency (TCF) and curie point (T_c) of 0.55, 0.48, 485, 240 pc/N, 1620, 0.0023, 1.1 kV/mm, 29.5 coul/cm^2, and 346 ^{o}C at sintering temperature 980 ^{o}C. With further increasing ZnO content the K_p, K_t would be decreased due to exceeding solubility of composition resulting in the more non-ferroelectric ZuO segregated in grain boundary to deteriorate the piezoelectric properties like the CuO-doped effect on hard piezoelectric material [4,9].

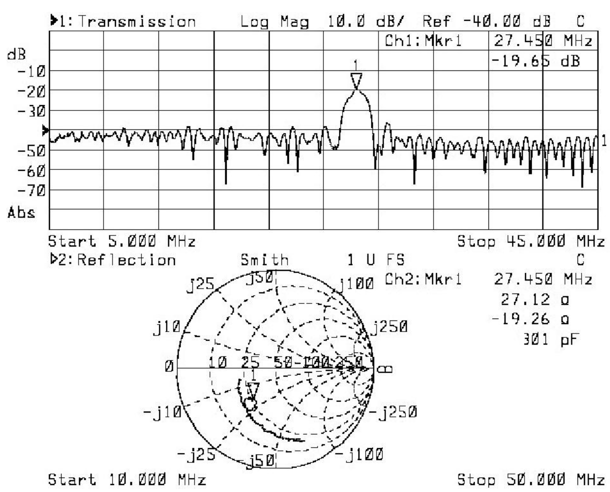

Fig. 3 The frequency response of SAW device fabricated on PMNZTC-Z10x ceramics substrate

To fabricate SAW device, the ceramics disc substrates with our preferable composition were polished to a mirror finish on one side with surface roughness below 0.1 μm. Then, aluminum electrode patterns, 0.3 μm thickness in the form of interdigital transducer (IDT), were applied onto the polished surface using the lift-off photolithographic process. Then, two IDTs were fabricated in the low-temperature sintered PMNZTC-Z10x ceramics substrate constituting basic SAW device. Results showed that the center frequency of 27.450 MHz leads to a phase velocity (V_P) of 2200 m/s and the insertion loss (IL) is about -19.65 dB shown in Fig.3. In addition, the effective coupling factor (k^2) is about 5.1 % obtained from the equation in reference [7]

4. Conclusion

In this study, we successfully use the ZnO doping in the PMNZTC-Z10x material system to lower the sintering temperature and simultaneously present good characteristics of the ceramics and further use these hard-type ceramics as substrates for the SAW devices. Results shows they have high k^2 (5.1%) and lower IL.

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