Intermediate Temperature Sintering of La-Modified $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ Piezoelectric Ceramics

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In order to realize the co-firing with Ag/Pd electrodes in multilayer devices, $Pb(Zn_{1/3}Nb_{2/3})_{1-x-y}Zr_xTi_yO_3$($0.25<x<0.35$, $0.25<y<0.35$) piezoelectric ceramics (hereafter designated PZN-PZT) modified by La_2O_3 has been prepared by conventional technique with sintering temperature from 1100°C to 1140°C. X-ray diffraction patterns demonstrated that pure perovskite phase was obtained. Secondary electron image (SEI) showed that crystalline grains in ceramics were well grown. d_{33} of manufactured sample was as high as 560×10^{-12}C/N. k_p was about 0.61 and tgδ about 30×10^{-3}. The existence of liquid phase examined by electron diffraction in PZN-PZT sample is beneficial to sintering of the ceramic.

1. Introduction

It is well known that the sintering temperature of conventional PZT-based piezoelectric ceramic is about 1250°C~1350°C. The microstructure and properties of ceramics are difficult to control because of the volatility of PbO during sintering at such high temperature. In addition, the high sintering temperature requires the use of expensive metals for internal electrodes in multilayer piezoelectric devices, therefore, lowering the sintering temperature is highly desirable to enable the ceramics to be co-fired with less-expensive metals in multilayer devices.

The low temperature sintering of PZT-based ceramics has been reported by many researchers using different methods, (1) Cationic substitutions in the ceramics[1], (2) Addition of low melting glass[2,3] and oxides[4], (3) Sintering using very fine and chemically active powder prepared by the sol-gel process[5] *via* oxalate precursors[6] or by partial chemical process[7]. These methods, however, are all degrading the properties of ceramics. Some compositions of the low melting glass are poisonous. Without deteriorating the properties of ceramics, a special firing process has been successfully applied without using any flux additives to manufacture the PZN-PZT piezoelectric ceramics at sintering temperatures 1100°C~1140°C. The sintered ceramics, with its high piezoelectric coefficient d_{33}, can be used in co-firing with Ag/Pd electrodes in multilayer piezoelectric devices such as a microactuator.

2. Experimental

The samples were prepared by using a conventional method of electric ceramic engineering. The commercially available Pb_3O_4, ZrO_2, TiO_2, $ZnCO_3$, Nb_2O_5, La_2O_3 were used as raw materials. The corresponding metal oxides of the prescribed amount were synthesized at 850°C for 2 h. Disk sample (Φ12 mm×1 mm) was sintered in 1100°C~1140°C for 0.5~10 h. All the samples were polarized at applied voltage of 3500 V/mm at 120°C in a silicone oil bath for 15 min.

The piezoelectric properties of samples were measured after being polarized and stabilized for 24 h. Piezoelectric coefficients were measured on a d_{33} meter. Planar coupling coefficient k_p was calculated from the resonance measurement. Curie temperature was measured by capacitance dependence of temperature with a X-Y recorder, where X-axis representing temperature and Y-axis representing capacitance. The bulk density ρ was measured by spilling method. Crystalline phase was identified by powder X-ray diffraction method. Microstructure of the specimen were analyzed by an electron probe microanalysis (EPMA-8705QH2, Shimadzu).

3. Results and Discussion

Figure 1 shows the relation between bulk density (ρ) of PZN-PZT and firing time at 1130°C. As shown in Fig.1, ρ increases quickly when the sintering time $t<1$ h, however, when the sintering time $t>1$ h, ρ increases much more slowly. The maximum density ρ is 7.86 g/cm^3, 98% of theoretical density.

Figure 2 depicts the XRD patterns of PZN-PZT piezoelectric ceramics sintered at 1130°C for 5 h. Pure perovskite phase was obtained for the sample, and the sintered sample was composed of both tetragonal and rhombohedral phase[8]. In a conventional sintering

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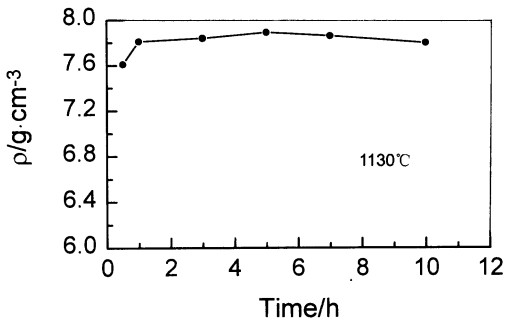

Fig.1 Relationship between sintering density and soaking time for PZN-PZT ceramics fired at 1130°C

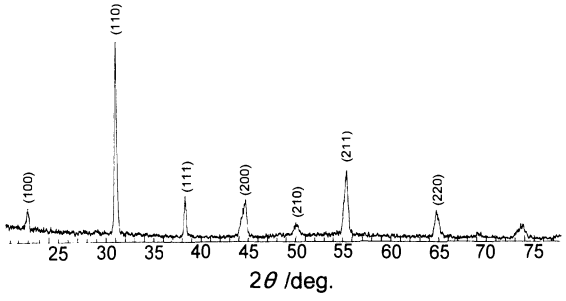

Fig.2 X-ray pattern of PZN-PZT sample sintered at 1130°C for 5 h

processing of PZN-based ceramics, pyrochlore phase often appears as a second phase which is harmful to dielectric and piezoelectric properties of piezoelectric ceramics. However, no pyrochlore phase was observed in these samples because of $PbTiO_3$ acting as perovskite seeds and stabilizing the PZN-PZT perovskite phase[9].

The secondary electron image of fracture of PZN-PZT is shown in Fig.3. Uniform microstructure was obtained for PZN-PZT samples sintered at 1130°C for 3 h to 7 h. Their grains grow well and average grain size was about 2~3 μm. But the grains did not grow well if the soaking time was less than 1 h as shown in Fig.3(a). It is noteworthy that grains stopped to grow after 5 h soaking at 1130°C.

Figure 4 shows the piezoelectric constant d_{33} as function of soaking time for PZN-PZT sample sintered at 1130°C. The d_{33} increased rapidly as the soaking time increasing in the initial period and saturated beyond 5 h. The d_{33} as high as 560×10^{-12} C/N was obtained for PZN-PZT sample sintered at 1130°C for 5 h.

The temperature dependence of dielectric constant ε (1 kHz) is shown in Fig.5. For sample sintered at 1130°C for 0.5 h, a broad and low dielectric peak was observed at 204°C. With the increase of soaking time, the grain size grew well, the dielectric peak became higher and sharper. The hysteresis loop is shown in Fig.6. The remanent polarization p_r of sample sintered at 1130°C for 5 h was greater than that for 0.5 h.

All these phenomena can be explained by grain growth processing. If the heating time at a constant temperature is short, the grain size is small, the ferroelectric polarization is clamped and difficult to reverse by electric field. As the grain grows with the increase of heating time, the domain reverse becomes more easily and ferroelectric properties become more dominant. Therefore, d_{33}, p_r and ε increase respectively. The properties of PZN-PZT piezoelectric ceramic sintered at 1100°C~1140°C is listed in Table 1. Comparing the results with the phenomena mentioned above, we can conclude that 5 h soaking at 1130°C is the most suitable condition for the intermediate temperature sintering of PZN-PZT ceramic.

The glass phase, which is helpful for the sintering of ceramics, was observed by electron diffraction and TEM (JEM-200CX) in the sample sintered at 1130°C for 1 h (Fig.7). However, no glass phase was found in

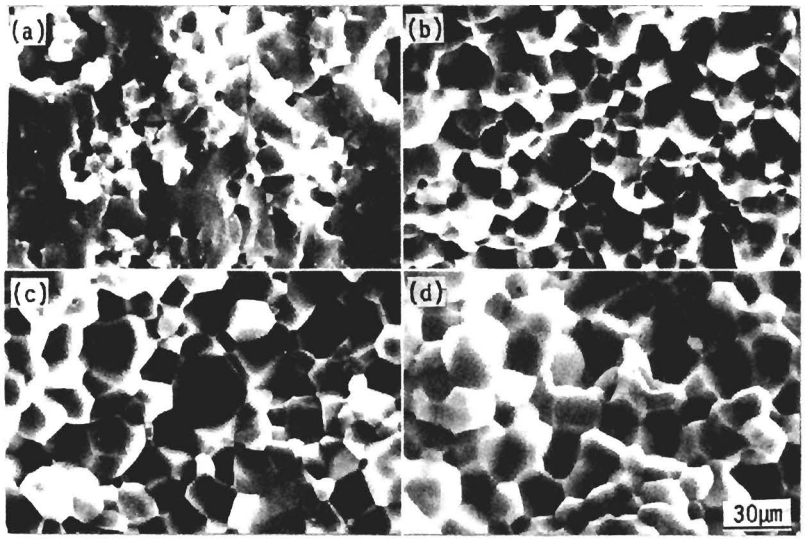

Fig.3 SEI micrograph of fracture of PZN-PZT samples sintered at 1130°C (a) 1 h, (b) 3 h, (c) 5 h, (d) 7 h

Table 1 Properties of PZN-PZT samples

Temp./°C	$\rho/(g/cm^3)$	k_p	$d_{33}/(\times10^{-12}C/N)$	$tg\delta/(\times10^{-3})$	$\varepsilon/\varepsilon_0$.
1100 (3 h)	7.81	0.57	477	27	2569
1130 (0.5 h)	7.61	0.48	400	28	2180
1130 (1 h)	7.81	0.54	448	27	2455
1130 (3 h)	7.84	0.60	522	27	2720
1130 (5 h)	7.89	0.61	560	24	2921
1130 (7 h)	7.86	0.61	559	22	2739
1130 (10 h)	7.80	0.58	560	22	2804
1140 (3 h)	7.86	0.60	550	25	2856

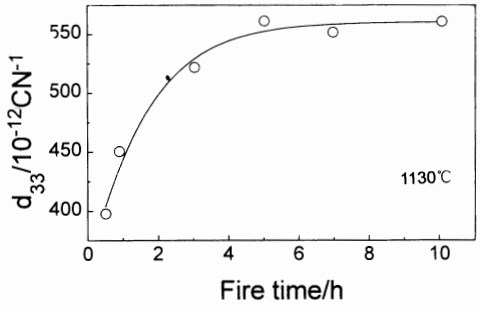

Fig.4 Relationship between d_{33} and soaking time

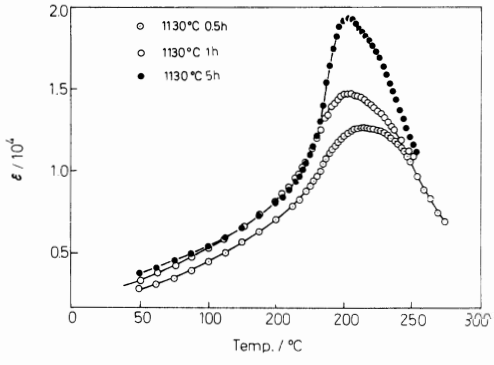

Fig.5 Relationship between dielectric constant and temperature for PZN-PZT samples at 1130°C

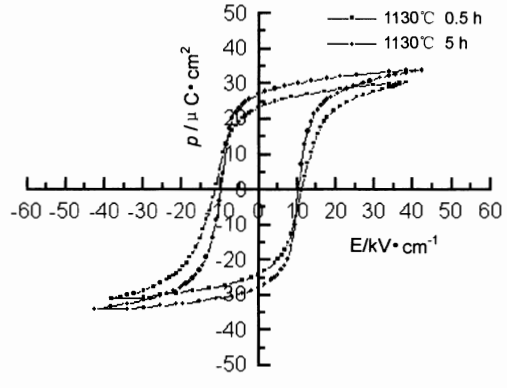

Fig.6 Hysteresis loop of PZN-PZT sample sintered at 1130°C

the sample of 7 h soaking at same temperature. EDS demonstrated that the glass phase were composed of

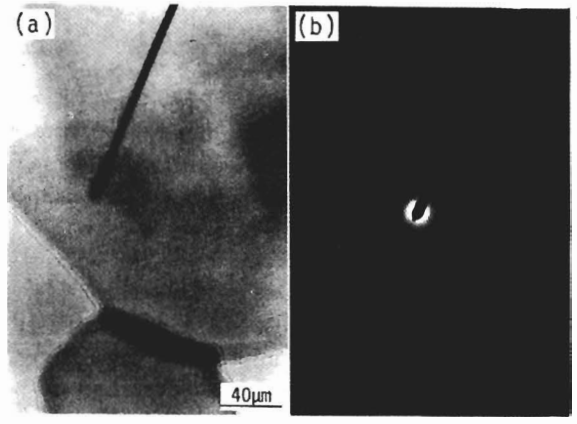

Fig.7 TEM image of liquid phase existing in PZN-PZT ceramics and its electron diffraction micrograph

Pb, O, Zr, Ti, Nb *etc.* It is believed that some low melting intermediate phases are produced in the early stage of sintering processing, and then enter into the lattice, thus having no influence on the properties of the PZN-PZT piezoelectric ceramic.

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