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Ceramics International 26 (2000) 541–544

CERAMICS INTERNATIONAL

The effect of microstructure on the pyroelectric properties of PZT ceramics

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Received 25 May 1999; received in revised form 6 July 1999; accepted 9 September 1999

Abstract

Lead titanate zirconate ceramics with a base composition $PbTi_xZr_{1-x}O_3$ with $x=0.07$ was pressure sintered, starting from mixed oxide powders. The effects of sintering time on the microstructure, on the dielectric constant and pyroelectric properties of the resulting ceramics are reported and discussed. It is found the pyroelectric properties are strongly influenced by sintering times and hence microstructure. The results indicate that as the grain sizes increase the dielectric constant and the Curie temperature increases, while the pyroelectric current decreases. The temperatures that the total pyroelectric coefficients due to primary and secondary effects change sign and directions of spontaneous polarization have been also reported. The measured pyroelectric coefficients show also some fluctuation, but for low temperature the samples with large grain size are more stable. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sintering; B. Grain size; D. PZT; Pyroelectric properties

1. Introduction

Since the discovery of a large piezoelectric and pyroelectric effect with a base composition of $Pb(Ti_xZr_{1-x})O_3$ ceramics [1–4], it has continuously been improved by different material variations. The pyroelectricity has been studied in both single-crystal and polycrystals [5,6], polymer [7](PVDF), glass-ceramic [8] and in thin films [9,10]. The word-wide research has been carried out to investigate the properties, preparation, characterization, and application such as pyroelectric detector, integrated optical modulators, infrared detectors and switching devices in the form of either bulk samples or thin films' ceramics.

The method of preparation and characterization of pyroelectric ceramics have been studied in details [3,6,11–14]. The pyroelectric parameters and measurement of pyroelectric coefficients have been reported in the literature [15–18], but the effect of microstructure and grain size on the pyroelectric properties have not been studied in details [19].

The pyroelectric coefficient p is defined as the differential changes in spontaneous polarization P due to a change in temperature and define as:

$$\Delta P_i = p_i \Delta T \tag{1}$$

where p_i is one, two, or three independent coefficients that together specify the pyroelectric vector $\vec{p}$. The total pyroelectric coefficient measured at uniform heated specimens and constant stress is the sum of the coefficient at constant strain that is so-called the primary coefficient and the piezoelectric contribution due to the thermal expansion is commonly described as secondary coefficient. The tertiary effect is caused by non-uniform heating of the specimens that creates local stress area and subsequent undesirable piezoelectric charge releases.

Due to the close interrelationship between the grain size, microstructure and electrical properties of pyroelectric ceramics there is a direct effect on both domain alignments during poling and domain wall relaxation after poling. The aim of this paper is to study the effect of pyroelectric properties on the grain size and on the microstructure. During the poling normally two types of domain switching in PZT pyroelectric grains is associate

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PII: S0272-8842(99)00092-9

with two different coercive fields and by depoling the ceramic we could observe also these orientations.

2. Experimental procedure

Lead titanate zirconate oxide with a base composition $Pb(Ti_xZr_{1-x})O_3$ with $x=0.07$ mixed and calcinated at 1000°C for 1 h. The samples are sintered at temperature of 1200°C with heating rate of 5°C/min and a cooling rate 5°C/min and soaking time held for five sets of specimens for a period of 1,3,7,9 and 11 h. Careful temperature control is maintained through the calcination and sintering cycle with a microprocessor controlled furnace model Labotherm HT 04/17.

The specimens were poled at 120°C in a bath of silicon oil. The poling was carried out for 30 min using an applied field of 20 kV/cm and then the specimens cooled to room temperature with the field applied.

The pyroelectric current was measured with Phywe Universal Measuring Amplifier [20] model 11761.93. This amplifier has two operating modes: for voltage sources of high resistance the electrometer mode with input resistance greater than $10^{13}\Omega$ and for very low measurement signal sources low drift mode is used. The signal can be amplified by several powers of 10, whilst a stable zero position of the signal is carefully maintained. In both modes, signals that are superimposed by higher frequency noise or other interference, can be smoothed using a low pass filter with selected time constants (0–3 s). A block circuit diagram for this measuring amplifier is shown in Fig. 1.

The electrical model of device and measuring amplifier is shown in Fig. 2. For measuring the pyroelectric current a measuring resistor was wired in parallel to the input, then current (I_{meas}) after amplification was measured as voltage drop at this resistor. The pyroelectric current (I_p) for this circuit is:

$$I_p = I_{meas}\left(1 + R_{meas}/R_p\right) \tag{2}$$

where R_p is the sample resistance. If the value of resistor R_{meas} is chosen much smaller than R_p then we can write

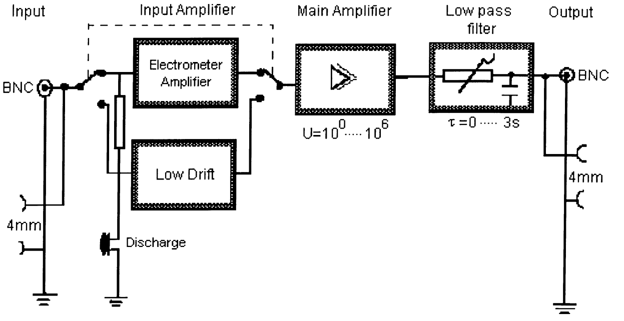

Fig. 1. Block circuit diagram for measuring amplifier.

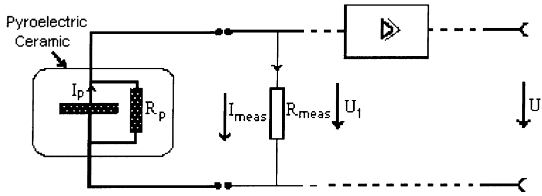

Fig. 2. The electrical model of device and measuring amplifier.

$I_p \approx I_{meas}$ and according to Ohm's low $I_{meas} = U_1/R_{meas}$ or I_p after amplification with factor A is:

$$I_p = U_2/(AR_{meas}) \tag{3}$$

where U_2 is the amplified output voltage.

The output voltage (U_2) was measured with a high resolution digital voltmeter. The typical value of R_p was about $\approx 3\times10^8\Omega$ and the value of R_{meas} was chosen to be $1.5\times10^6\Omega$. The current error $\Delta I_p/I_p$ including the effect of variations of R_p was found to be $\Delta I_p/I_p \leqslant \pm 0.081$.

The temperature measured with a high resolution (0.1°C) microprocessor-based digital thermometer model Fluke-51. An external k-type thermocouple with a tolerance ±1.1°C over the range of 0 to 250°C is used as temperature sensor.

3. Results and discussion

In Table 1 the measured average grain size (l_{av}) and densities (ρ) are shown. The grain sizes were observed from SEM photograph, and microstructure parameters were determined by the Heyn intercept method [21]. The Curie temperature (T_c) and the temperatures that the total pyroelectric coefficient (p) changes sign were measured from depolarization procedure as describe later.

In Table 1, $\sigma(l_{av})/l_{av}$ are the variance and define as:

$$\sigma = (1/N)\sum_{i=1}^{N}\sqrt{(X_i - X_{av})^2} \text{ and } X_{av} = (1/N)\sum_{i=1}^{N}N_{x_i} \tag{4}$$

Table 1
The sintering time and grain size for five sets of samples

Samples	Sintering time (h)	Density $\rho \pm 0.1$ gr/cm^3	Average grain size		Curie temperature $T_c \pm 2$°C	Total p change sign at (°C)
			l_{av}(μm)	$\sigma(l_{av})/l_{av}$		
A1	1	6.43	3.97	±0.02	193	74
A2	3	7.23	8.59	±0.03	195	77
A3	7	7.56	13.13	±0.04	200	79
A4	9	7.60	15.68	±0.08	206	82
A5	11	7.64	16.29	±0.10	210	84

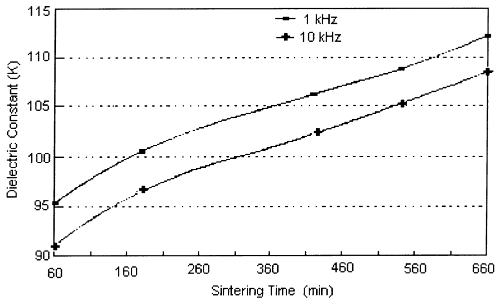

Fig. 3. The dielectric constant as function of sintering time.

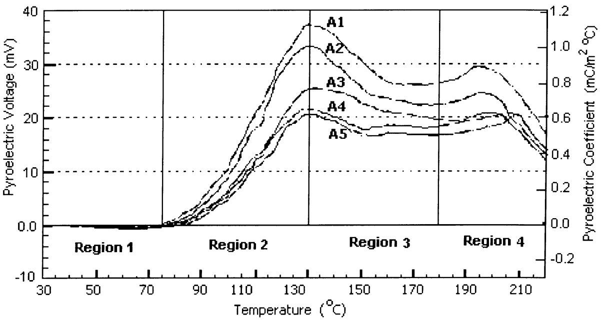

Fig. 4. The pyroelectric voltage and coefficient as function of temperature.

where N is the number intersection of test line with the grain boundary.

Fig. 3 shows the dielectric constants (K) as function of sintering time at frequency of 1 and 10 kHz. The K values vary from 95.04 for sample A1 (smallest grain size) to 112.15 for sample A5 (largest grain size) at 1 kHz and from 91.08 to 108.15 at 10 kHz.

The total output pyroelectric voltage measured by circuit Fig. 2 with gain factor $A = 10^3$ as function of temperature is shown in Fig. 4. The temperature dependence of the total pyroelectric coefficient at constant stress is determined by the combination of primary (p_1) and the piezoelectric contribution due to the thermal expansion (secondary coefficients, p_2). There are four distinguishable and significant regions that associated with different phenomenon's. In region 1 (between 30 and 75°C) the changes in depolarization with temperature are small hence the pyroelectric voltage is small. In this region the relative sense of p_i may be seen to change sign about 70–80°C that the absolute sense is dependent on microstructure. The measurement result for each sample is shown in Table 1. As the temperature rise, region 2, (between 75 and 130°C) the dipoles get enough energy to move and change the polarization and pyroelectric voltage increase and maximum depolarization occurs about 130°C that associated also with 90° domain's direction in orthorhombic structure. In region 3, (between 130 and 180°C) again the pyroelectric voltages start to decrease as we expected.

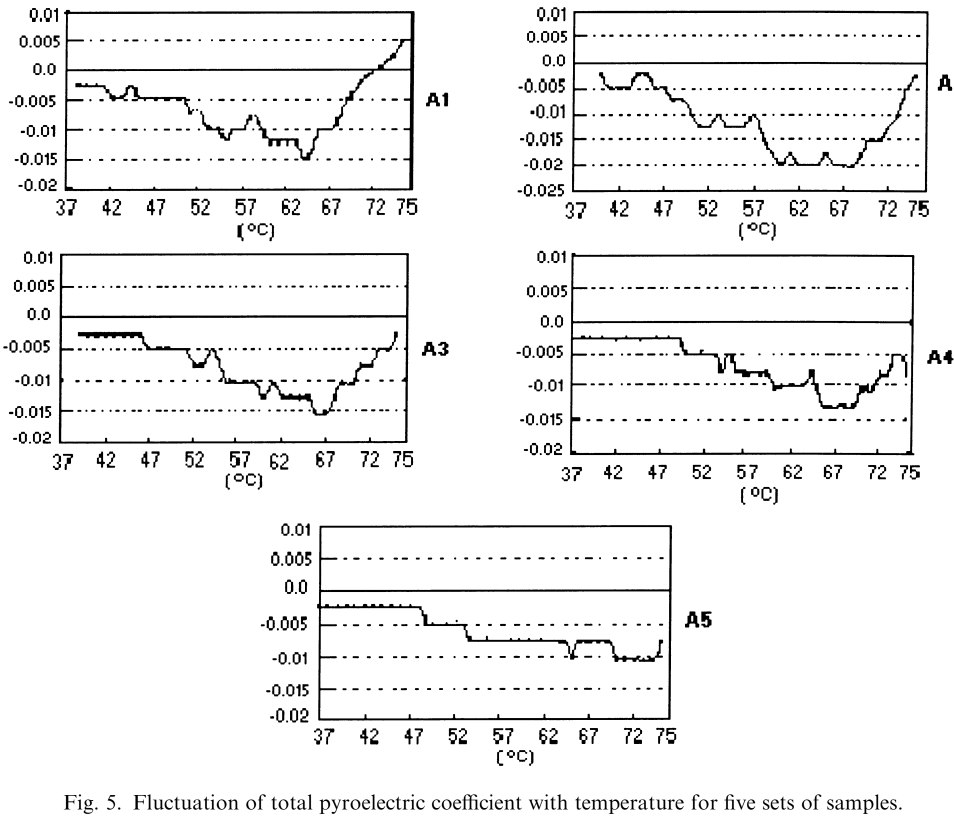

Fig. 5. Fluctuation of total pyroelectric coefficient with temperature for five sets of samples.

By increasing the temperature, region 4, the structure changes and the rhombhedral phase become dominant and second depolarization associated with this structure is occur. The maximum pyroelectric voltages in this region vary with temperature, for sample A1 has the maximum value that occurs at temperature 193°C ± 2. This peak value starts to decrease for other samples and lowest value associated to temperature 210°C ± 2 for sample A5. If we take this peak as Curie temperature, the measured Curie temperatures with other parameters are shown in Table 1. By increasing temperature further, the pyroelectric voltage will decrease.

The measured results as shown in Fig. 5 indicate the total pyroelectric coefficients have a fluctuation with temperature, although this fluctuation is small, but at low temperature the pyroelectric coefficient for large grain size samples more stable than small grain size, since the samples with small grain have more freedom to move with temperature.

4. Conclusion

The measured average grain size (l_{av}), density (ρ) and dielectric constants (K) are increase as the sintering time increase. By depoling the samples the measured Curie temperatures increase while the pyroelectric voltage decrease with sintering time. The temperature associated with change sign in total pyroelectric coefficient increase with grain size. Two domain directions can be revealed, one corresponds about 130°C with 90° domain direction in orthorhombic structure and the second depends on the sintering time vary from 193°C for smallest grain size to 210°C for largest grain size correspond with rhombohedral structure domain direction. The pyroelectric coefficient fluctuates with temperature, but for large grain size up to about 47°C are more stable.

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