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Electrical investigation of sintering factors influence on PLZT ceramics

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Abstract

The role of technological factors like calcining and sintering temperature on the dielectric, electromechanical, ferroelectric and piezoelectric properties of PLZT 9/65/35 ceramics has been investigated. This composition has been chosen because it shows the coexistence of normal micron-sized polar domains with nanodomains and it is therefore very sensitive to thermal history. The samples have been prepared by a conventional mixed oxide method followed by sintering in Pb-rich atmosphere, so that only B-site vacancies have been obtained. For all sets of samples the variation of technological parameters induced changes in the physical properties. A relatively high variation of the dielectric permittivity and field-induced strain has been found among samples sintered at different temperatures. These variations have been connected with the microstructural parameters (grain dimensions and distribution) found from SEM analysis.

Keywords: Dielectric properties; Ferroelectric properties; PLZT; Relaxor ferroelectrics; Sintering

1. Introduction

La-modified lead zirconate–titanate ceramics (PLZT) are very interesting materials as they undergo the normal ferroelectric to relaxor transition at a certain La-content whose value depends on Zr/Ti ratio.[1] This behaviour is due to the introduction of vacancies at A- or B-sites of the perovskite structure, with the consequent disturbance of the ferroelectric order. At high La contents the decoupling of the BO_6 octahedrons may be strong enough to substitute the long range ferroelectric order (micron-sized domains) with a nanopolar domain state characterized by relaxor behaviour. Relaxors are characterized by the frequency dispersion of the complex permittivity, a broad dielectric peak, high dielectric constant, small electromechanical hysteresis and high electro-optical coefficients, which make them very attractive materials for a wide range of applications like multilayer ceramic capacitors, electro-optical devices, ultrasonic and medical imaging devices.[2]

While many theoretical and experimental papers have been dedicated to the influence of La substitution on the relaxor properties of PLZT system, much less attention has been dedicated to the influence of technological factors (calcining and sintering temperature and time, sintering atmosphere etc.). By examining results reported in literature on similar compositions of PLZT[3,4] we have noticed that there are relevant differences even among nominally identical compositions. This can arise obviously from hidden compositional differences, knowing that the phase diagram of the PLZT system is very sensitive to small variations in the ratio of Zr/Ti and/or La content. But nevertheless a great amount of differences can arise from the distribution of vacancies over the A- and B-sites which are finally due to different technological parameters. Many results have been published on the PLZT system which is one of the most intensively studied, due to its importance for modern applications,[1–4] but less accent has been put on this aspect. The object of this work is to investigate the role of some of the preparation conditions such as calcining and sintering temperature on the ferroelectric, electrostrictive, piezoelectric and dielectric behavior of a selected composition: PLZT 9/65/35, where the first of the three numbers refers to the La content in at.% and the last two represent the ratio Zr/Ti. This composition is a very interesting one since it is near the boundary between relaxor (*R*) and normal ferroelectric (nFE)

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behavior. Therefore it shows mixed relaxor–ferroelectric behavior and a peculiar sensitivity to thermal treatment.

2. Experimental

PLZT 9/65/35 ceramics were prepared by a conventional mixed oxide method, according to the formula $Pb_{1-x}La_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$ ($x=0.09$). The purity of the oxides used for preparation was 99.9%. The oxide powders were wet ball milled with zirconia balls in the stoichiometric amount for 24 h, the suspension was then freeze dried, calcined for 4 h at temperature 800 °C (this set of samples was conventionally called "80") or 850 °C (set of samples "85"), sieved at 250 μm and uniaxially pressed at 30 MPa (few samples were isostatically pressed at 300 MPa) into disks (diameter 22 mm, thickness 2 mm). The relative green density of the samples was about 65%. The sintering process was also varied for different sets of samples. Some sets have been sintered at 1200 °C ("12") for 2 h. Others have been subjected to a further sintering treatment at 1300 °C ("13") for 2 h to enhance grain growth and to reduce the defects density. The sets of samples which are discussed here are of the type "80–12" (calcined at 800 °C, sintered at 1200 °C), "85–12" (calcined at 850 °C, sintered at 1200 °C) and "85–13" (calcined at 850 °C, sintered at 1200 then at 1300 °C). Their physical characteristics (green density, final density etc.) are shown in Table 1.

X-ray diffraction patterns, taken on calcined powder and sintered samples, were recorded using CuK_β radiation at room temperature.

The sintered samples have been polished, cleaned and screen printed with silver electrodes. As the samples are presumably near the boundary ferroelectric–relaxor, they still retain some ferroelectric behavior. In order to investigate their piezoelectric properties, some of the samples have been poled in high electric field (dc field of 3 kV/mm for 40 min at 120 °C into silicon oil). The dielectric response was obtained by using a HP 4194 A impedance bridge which can cover a frequency range between 100 Hz and 40 Mz, in a four-wire configuration. The level of the signal was 0.5 V/mm to ensure small-signal dielectric properties.

In order to characterize the displacement behavior a capacitive displacement sensor was used; the sample mounting and test conditions are described elsewhere.[5] The ferroelectric behavior has been characterized by using a Sawyer–Tower type device.

For temperature measurements, the samples were placed in a Delta Design 9023 A test chamber, which can be operated between −180 °C and 315 °C. The temperature was measured using a HP 34401A multimeter via a Pt resistance thermometer mounted directly on the ground electrode of the sample fixture. A four wire configuration was used to measure the resistance of the Pt thermometer in order to increase the accuracy of the temperature. The sample temperature could be monitored with an accuracy of 0.1 °C. Before measurements, the samples were thermally treated at a temperature much higher than that corresponding to the dielectric maximum (T_m) to remove the effects of aging and electric history. Data were taken both on cooling and on heating the samples at a rate of 1 °C/min. It was found that the cooling/heating rate has a great influence on the obtained dielectric response and that higher rates can hide relevant features in this peculiar system where the slowing down of the order parameter dynamics, which causes freezing of the fluctuating polarization into a quasi-static precursor ferroelectric domain, stabilized on large time scales.

3. Results and discussion

The X-ray diffraction results show that a pure perovskite structure was formed, without any pyrochlore phase presence. Mean grain sizes taken from SEM micrographs of two typical samples from the sets 85–12 and 85–13 (80–12 has only small microstructural differences with respect to 85–12 therefore is not shown here) are reported in Table 1. It can be observed that much larger grain sizes are obtained for the samples 85–13 which are sintered at higher temperatures for longer time.

Dielectric hysteresis (P–E) loops for the samples are shown in Fig. 1. The values of P_s, P_r and the coercive field E_c can be seen to be more or less similar, somewhat higher for 85–13 sample. It would appear that the

Table 1
Physical properties of the PLZT 9/65/35 sets of samples considered for the experiment[a]

Sample	Relative green density (%)	Relative final density (%)	Grain size (μm)	T_m (°C)	ε_m (100 Hz)	ε_{RT} (100 Hz, 25° C)	Max. strain (%) (190 kV/cm)	d_{31} (pC/N)	c_{33}^E (10^{10} N/m^2)
80–12	64.9	95.9		95.2	6892	4887	0.115	−53	11.8
85–12(1)	64.7	94.0		90.1	7088	4970	0.126	−79	7.8
85–12(2)	65.0	96.6	1.5	80.5	7000	5213	0.133	−51	14.3
85–13	65.0	96.6	3.3	86.5	8290	6000	0.32	−56	14

[a] Sample names are related to their calcining and sintering conditions (see text). 85–12 (1) and (2) sets refers to samples prepared at the same calcining and sintering temperatures and time, but with slight differences in their ball milling conditions.

specimens are ferroelectric, however the slim-loop nature of their P–E curves suggests that most of the aligned dipole movements switch back to a randomly oriented state upon removal of the field. Indeed, polar nanodomains result into correspondingly slim loop-like P–E curves with only small remanent polarizations. Two causes could be responsible for the weak double loop which is observed for all the samples: stabilization of an antiferroelectric state in rhombohedral PLZT by La content or pinning of domain states by defects. We would rather adopt the first hypothesis, since in our case all samples, despite their different thermal treatment, presented this feature.

Fig. 2 shows the field-induced strains for the different sets of samples. The magnitude of the maximum field-induced strain was higher (0.32%) for the 85–13 samples than for the others (0.11–0.13%). The shape of curves evidences a mixed relaxor-ferroelectric behavior, since characteristics of both phases are evidently preserved. The higher values of the maximum strain in 85–13 samples are probably related to the existence of some normal sized ferroelectric domains (favored by the existence of larger grains). They can increase the strain by enhancing the ease of polarization switching. In the other samples polarization changes probably occur mostly by the movements of nanopolar domains rather than by switching of normal domains, therefore a smaller strain is obtained. The remnant strain is small for all specimens, as can be observed in Fig. 2. From the shape of the curves it can be seen that the coercive field for all the samples do not show a definite value but a range in which domains start to align with the electric field.

On some samples we have performed also piezoelectric measurements. The samples preserved a metastable polar state (on a large scale time) after poling at high electric fields as demonstrated by piezoelectric d_{31} constant values evaluated from resonant measurements (Table 1). Strictly speaking, these d_{31} values are only indicative for the sample properties, since their values slightly modifies in time due to polarization relaxation towards equilibrium values.

The dielectric response (real permittivity and loss factor) is plotted in Fig. 3 for sample 85–13 (similar behaviour has been found for the other samples with slight variations in peak positions and intensities which are shown in Table 1). All the samples showed pronounced relaxor ferroelectric behavior, characterized by strongly diffuse dielectric peaks and shift of permittivity maxima towards higher temperatures with increasing measurement frequency. The corresponding loss factors, presented on the lower part of the graph (open symbols) also exhibit relaxor behavior.

Some interesting features are observed in these samples which are different from what has been reported in literature up to now.[1–4] The graphs show the temperature dependence of the dielectric permittivity and loss factor for both cooling and heating measurements. On cooling the permittivity exhibits strong dispersion both before and after T_m, while results previously reported[1–4] show dispersion only for the low temperature part. Moreover a small peak (more evident in 85–13 samples) which does not shift with frequency is observed below T_m, at about 48 °C. On heating, this peak increases intensity and shifts at about 35 °C thus presenting thermal hysteresis. This behavior could be attributed to the particular composition of the system, which results into a mixture of ferroelectric and relaxor phases. Thus the peak which arises at 48 °C on cooling and 35 °C on heating could be attributed to a transition R-nFE and nFE-R, respectively. A somehow similar behavior has been observed in other PLZT systems, but at higher La content. We believe that the differences are associated with the various preparation methods which reflects in a different distribution of A and B-site vacancies, as well as to a different amount of oxygen vacancies.

The loss factor shows dispersion on all the temperature ranges and a strong difference among cooling and heating is evidenced below T_m: while on cooling a step

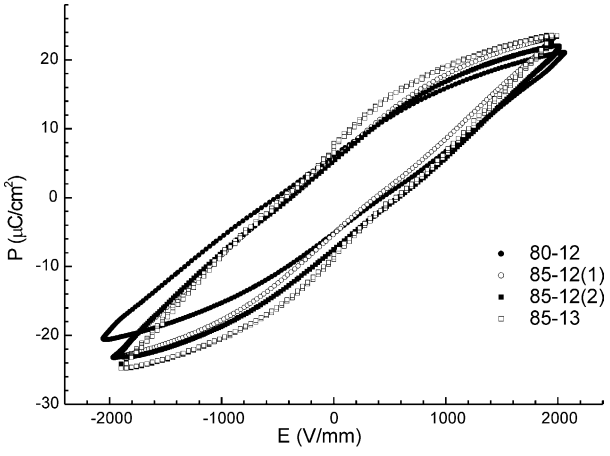

Fig. 1. Dielectric hysteresis loops for the different sets of samples.

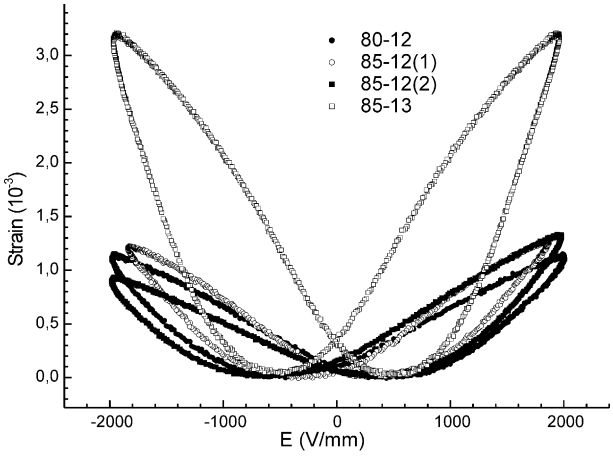

Fig. 2. Field-induced strains for the different sets of samples.

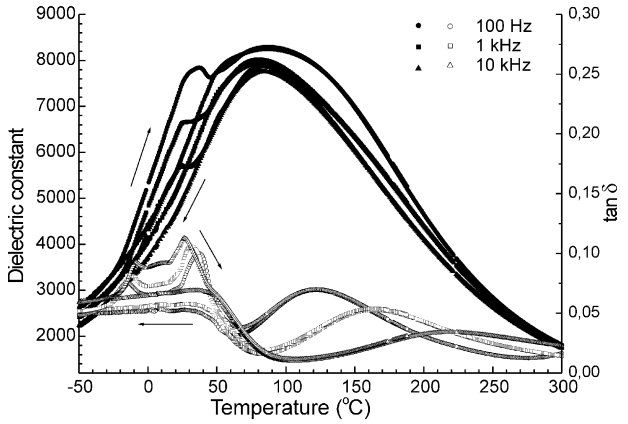

Fig. 3. Dielectric response (real permittivity—upper curves and loss factor—lower curves) of a 85–13 sample, measured at different frequencies on cooling and heating (at 1 °C/min), as shown by the arrows.

behavior is obtained, on heating a few peaks are observed. The step decrease is normally observed in relaxor materials. One of the peaks occurring on heating could be associated with the transition nFE-R, but for the other peaks we do not have yet an explanation. Another peculiar feature is a peak in the high temperature part which does not show thermal hysteresis but strong dispersion with frequency. This peak could be due to the movement of nanodomains dispersed in the paraelectric matrix above T_m with the applied electric field. It seems that this type of relaxation (which was not previously observed in this composition) needs a relatively low activation energy, since it occurs at relatively low temperatures: about 120 °C (100 Hz) shifting then to about 165 °C at 1 kHz and 225 °C at 10 kHz for the 85–13 sample. In the sample 85–12 which was sintered at lower temperature for shorter time, the inherent higher amount of defects could have produced pinning of nanodomains thus leading to higher activation energies, as reflected by the higher values of peaks temperatures (about 140 °C at 100 Hz, 180 °C at 1 kHz and 240 °C at 10 kHz).

The maxima of the dielectric constant ε_m, which are reported in Table 1 together with other relevant quantities such as room temperature permittivity ε_{RT} and T_m are comparable with other results reported in literature for ceramic 9/65/35 PLZT with B-site vacancies. However the permittivity peak is much broader therefore ε shows less variation with T which could be of advantage for certain applications. It can be observed that the best value of ε_m is obtained for the sample 85–13 which was sintered at higher temperature for longer time. Also the increase of calcining temperature from 800 to 850 °C produces some increase of ε_m.

4. Conclusions

In this work we have investigated the influence of technological parameters on PLZT ceramics with 9/65/35 composition and B-site vacancies. We have evidenced that the dielectric behavior of the samples is extremely dependent not only on the composition, but also on the sintering treatment. Significant variations have been also observed among the electrostrictive, piezoelectric and ferroelectric properties. Other differences are introduced also by the calcination treatment but the extensive discussion of all these factors as evidenced by detailed studies of X-ray diffraction, microstructural studies and dielectric spectroscopy measurements would require a much more detailed discussion and is therefore left for a further presentation.

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