Effect of sintering condition on properties of Cr-doped $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ ceramics

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Abstract. The effects of sintering temperature (T_{sinter}) and sintering time (t_{sinter}) were investigated for $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + x\%\text{wtCr}_2\text{O}_3$ system to determine the optimum regimen of sintering. The study was performed by determining the following parameters: relative density (ρ_{rel}) and sintering rate ($\dot{\epsilon}_{\rho}$). The grain size was diminished when small amounts of Cr_2O_3 were added to system and was enhanced when the sintering temperature and time was increased. The dielectric constant becomes maximum and the electric loss becomes minimum with the sintering temperature of 1290°C. The optimum regimen of sintering is $T_{\text{sinter}} = 1290^\circ\text{C}$ during 70 min. The piezoelectric properties for the optimum regimen of sintering were studied.

Keywords. Ceramics; chemical synthesis; dielectric properties.

1. Introduction

The properties of piezoelectric (most of them are also ferroelectric) ceramics are strongly influenced by their manufacturing procedures. Although the material compositional control is usually excellent, properties of the resulting ceramics are not necessarily good if improper processing conditions are used (Xu 1991).

The fabrication of piezoelectric ceramics includes the following steps: weighing of raw materials; ball milling; calcining; secondary grinding; shaping by mould-pressing or roll-pressing; removal of polymer paste; sintering; electrode coating; poling and characterizing (Xu 1991). After sintering process, the ceramic products are densified, therefore, in actual practice, the process is very complex. The sintering temperature and time are two parameters very important in the sintering process because by varying both parameters we can obtain ceramic systems with different properties. The density of a ceramics is affected by the sintering temperature and time in a more complex fashion. If the sintering temperature is too high or the sintering time too long, the density of the ceramics will be reduced owing to PbO evaporation at high temperatures. Celi *et al* (2002) reported the effect of sintering temperature on the dielectric constant (K), dielectric losses ($\text{tg}(\delta)$), Curie temperature (T_{C}), Curie constant, electromechanical coupling factors (k_{p} , k_{t} , k_{31}), planar and transversal piezoelectric coefficients (d_{33} , d_{31}) in PZT

ceramics. Seo *et al* (2004) studied the sintering behaviour and piezoelectric properties of the $\text{Pb}(\text{ZrTi})\text{O}_3$ – $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ system. He *et al* (2001) investigated the piezoelectric properties and microstructure of the $\text{PbZr}_x\text{Ti}_y(\text{Mn}_{1/3}\text{Nb}_{2/3})_{1-x-y}\text{O}_3 + \text{Cr}_2\text{O}_3$ system using two sintering temperatures. Dimitriu *et al* (2004) studied the piezoelectric and optical properties of the PT–PZ– $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics sintered at four temperatures.

The effects of sintering temperature and time on different properties of the $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + x\%\text{wtCr}_2\text{O}_3$ (PSZTC) system were investigated.

2. Experimental

The general formula of the materials studied was $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + x\text{Cr}_2\text{O}_3$, where $x = 0.0, 0.1, 0.2, 0.5$ wt% (abbreviated as PSZTC $x/53/47$). The samples were prepared by conventional processing method using mixed oxide powders. Reagent-grade oxide powders, PbCO_3 , ZrO_2 , TiO_2 , SrCO_3 , and Cr_2O_3 were used as the starting materials.

The reagent powders were milled during 120 min and calcined at 90 min in air. After drying, the powders were made into pellets and sintered at different temperatures (1200, 1245, 1290 and 1335°C) and times (70, 100 and 130 min). Electrodes were fabricated on the parallel faces of a previously cut cylinder by using an organosilver paste.

The macroscopic studies of sintered samples were analysed using two parameters: (i) relative density, $\rho_{\text{rel}} = \rho/\rho_{\text{T}}$,

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where ρ is the density of the sintered sample and ρ_T the theoretical density and (ii) sintering rate $\dot{\epsilon}_\rho = \dot{\rho}/\rho$, where $\dot{\rho}$ is the derived density.

Scanning electron microscopy (SEM) was carried out on fragmented samples in a microscope, JSM-5800. The dielectric constant and dielectric loss were measured at room temperature and was carried out by using a LCR bridge Quadtech 1750.

3. Results and discussion

3.1 Sintering of PSZTC ceramics

The relative density of the PSZTC specimens as a function of the sintering time at several sintering temperatures are shown in figure 1. The density must increase with sintering time until it reached a stable value (Durruthy *et al* 2001). In our case the density remains around 93 % for samples $x = 0.0$, 0.2 and 0.5 sintered at 1245, 1200 and 1290°C, respectively. The low density is related to

the low reactivity of the powders used as a raw material. However, the Cr doped modified lead zirconate titanate ceramics have piezoelectrics properties that make them suitable for device application. All samples are pure phase perovskites and the peaks belong to tetragonal phase. It is worthy to note that, from $x = 0$ to $x = 0.5$ all spectra show no evidence of pyrochlore phase.

ρ_{rel} did not show notable changes with increasing sintering temperature, however, the samples sintered at 1335°C were lower than the samples sintered at other temperatures. This may be due to PbO evaporation at high temperatures. For the samples sintered at 1200 and 1245°C the highest relative densities were obtained in the PSZTC 0.2/53/47 while for 1290 and 1335°C the highest relative densities were obtained in the PSZTC 0.5/53/47.

The sintering rate of the PSZTC specimens as a function of the sintering time at different sintering temperatures are presented in figure 2.

The sintering rate represents the densification of the material during the sintering process. As the sintering time was increased, the sintering rate decreased markedly,

Figure 1. Relative density as a function of the sintering time for several sintering temperatures and compositions.

Figure 2. Sintering rate as a function of the sintering time for several sintering temperatures and compositions.

Figure 3. SEM micrographs of the fractured surface of the PSZTC 0.5/53/47 samples sintered at (a) 1245°C/70 min and (b) 1290°C/70 min.

reaching negative values in some cases (around 100 min). These negative values indicate that the ceramic lost mass or was expanded, which can be attributed to PbO evaporation during the process. This suggests that the PSZTC specimen can be sintered at lower times (~70 min).

As shown in figure 3, the sample PSZTC 0.5/53/47 sintered at 1290°C has a relatively uniform grain structure with a grain size of ~2.3 μm (figure 3b and table 1), the sample PSZTC 0.5/53/47 sintered at 1245°C, on the other hand, have small grains with size of ~1.7 μm; some intragrain pores are also present (figure 3a and table 1).

Table 1. Grain size values of the PSZTC 0.2/53/47 and 0.5/53/47 for two sintering temperature and time.

PSZTC $x/53/47$	Grain size (μm)			
	$T_{\text{sinter}} = 1245^{\circ}\text{C}$		$T_{\text{sinter}} = 1290^{\circ}\text{C}$	
	$t_{\text{sinter}} = 70 \text{ min}$	$t_{\text{sinter}} = 100 \text{ min}$	$t_{\text{sinter}} = 70 \text{ min}$	$t_{\text{sinter}} = 100 \text{ min}$
0.2/53/47	2.9	3.2	3.1	3.5
0.5/53/47	1.7	1.9	2.3	2.7

Figure 4. SEM micrographs of the PSZTC $x/53/47$ ceramic system with (a) $x = 0.5$ (sintered at $1290^{\circ}\text{C}/70 \text{ min}$), (b) $x = 0.5$ ($1290^{\circ}\text{C}/100 \text{ min}$), (c) $x = 0.5$ ($1290^{\circ}\text{C}/130 \text{ min}$), (d) $x = 0.2$ ($1290^{\circ}\text{C}/70 \text{ min}$), (e) $x = 0.2$ ($1290^{\circ}\text{C}/100 \text{ min}$) and (f) $x = 0.2$ ($1290^{\circ}\text{C}/130 \text{ min}$).

SEM analysis (figure 4) evidenced the strong influence of Cr on the grain size and morphology. Grains were smoother and smaller as chromium concentration was increased. This inhibitor behaviour on grain growth has been previously reported for chromium in different ceramic systems (Wu *et al* 1992; Whatmore *et al* 2003).

It is known (Xu 1991) that the hard doping ions (such as chromium) also inhibit grain growth due to the low solubilities of these ions in the lattice of the solid solution. As a result, a portion of the doping oxides precipitate out of the normal grains and stay at grain boundaries, which subsequently resist the grain growth.

The grain size increased with increasing sintering time (figure 4 and table 1). For sintering time larger than 70 min, small pores were detected and heavy grains were seen for the PSZTC 0.2/53/47 specimen.

Figure 5 shows (a) the dielectric constant and (b) the loss tangent at 5 kHz at room temperature of the PSZTC $x/53/47$ samples.

The loss decreased and the dielectric constant increased with increasing sintering temperature. At 1290°C , there is a tendency for the loss to minimize and for the dielectric constant to maximize, similar results have been obtained by other investigators (Celi *et al* 2002; Seo *et al* 2004).

The increase of the sintering temperature produces increase of the grain size, and therefore, the domain size (Celi *et al* 2002) giving rise to a decrease of the domain density. This situation implies a minor number of mobile domain walls and as a consequence minor mechanical friction, minor dielectric loss. The increment of the domain size with the sintering temperature contributes to the increase of the dielectric constant, as a measure of the number of polarization unit cells (Celi *et al* 2002).

Figure 5. Dielectric constant and dielectric losses at 5 kHz as a function of the sintering temperature for several compositions.

Figure 6. Dependence of the electromechanical coupling coefficient, k_p , the piezoelectric coefficients, d_{31} , g_{31} and the mechanical quality factor, Q_m , on the amount of Cr_2O_3 for $Pb_{0.95}Sr_{0.05}(Zr_{0.53}Ti_{0.47})O_3$ ceramics sintered at 1290°C for 70 min.

The decrease of the dielectric constant with the sintering temperature increases for 1290–1335°C and could be related to PbO losses.

The PSZTC $x/53/47$ specimen can be sintered at 1290°C during 70 min.

3.2 Piezoelectric behaviour

With ceramics sintered at 1290°C for 70 min we studied the piezoelectric properties. Figure 6 shows the changes in the electromechanical coupling coefficient k_p , piezoelectric coefficients, d_{31} , g_{31} and the mechanical quality

factor, Q_m , as a function of Cr_2O_3 addition. As can be seen, k_p , d_{31} and g_{31} show a similar variation with increasing Cr_2O_3 content and Q_m increased from about 40 without doping to about 250 at 0.5%wt doping.

k_p , d_{31} and g_{31} increase with the amount of Cr_2O_3 when its concentration is lower than 0.2 %wt and decrease rapidly with further addition of Cr_2O_3 . These characteristics in PZT ceramics modified by Cr_2O_3 in its low concentration region are similar to what was observed by other investigators. This suggests that the anomalous properties may universally exist in PZT-based ceramics doped with stabilizers such as Cr in their low concentration regions (He *et al* 2001).

It is known that the formed oxygen vacancies, resulting from the substitutions of (Ti, Zr)⁴⁺ by acceptor Cr³⁺ ions, inhibited the movement of ferroelectric domain walls and resulted in the decrease of k_p , d_{31} and g_{31} .

4. Conclusions

The relative density and the sintering rate revealed better values at 70 min. With increment in the Cr content, the size and morphology of the grain underwent a change; the grain was smoother and the grain size was decreased. The grain size increased with increased sintering temperature and time. The dielectric constant showed a maximum at 1290°C and the dielectric loss showed a minimum at the same temperature. The sintering temperature and time required for full densification of the PSZTC system were 1290°C and 70 min, respectively. Finally the PSZTC 0.2/53/47 shows better piezoelectric properties for device application.

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