



Dielectric characterization of microwave sintered lead zirconate titanate ceramics



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ABSTRACT

Highly reactive lead zirconate titanate powders (PZT) with different compositions were successfully synthesized by the oxidant-peroxo method (OPM) and used to prepare dense ceramic samples with composition near to the *morphotropic phase boundary* (MPB) sintered at 1000 °C for 2 h using a tubular conventional oven and a commercial microwave system. Crystalline phases were identified in the powder and ceramic samples by X-ray powder diffraction and FT-Raman spectroscopy at room temperature. The fractured surface of the ceramic sample showed a high degree of densification with fairly uniform grain sizes. Dielectric constants measured in the range from 30 to 500 °C at different frequencies (1, 10 and 100 kHz) indicated a normal ferroelectric behavior regardless of the sintering method. Samples sintered by a microwave radiation (MW) method and composition near to the MPB region showed a maximum dielectric constant of 17.911 and an anomalous high Curie temperature of 465 °C.

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1. Introduction

Polycrystalline lead zirconate titanate (PZT) has attracted considerable attention due to its technological importance and versatile properties, particularly in the so-called *morphotropic phase boundary* (MPB) region that occurs at nearly equal concentrations of Ti^{4+} and Zr^{4+} . In this region, piezoelectric coefficients and dielectric constants exhibit an anomalously sharp maximum during the transition from Ti-rich tetragonal to Zr-rich rhombohedral phases [1]. The traditional route to obtain PZT involves reactions between metal oxides or carbonates at high temperatures [2,3]. However, this technique suffers from a number of uncertainties and drawbacks that result in severe stoichiometry deviations. The presence of impurities in raw materials, the lack of homogeneity due to poor mixing as well as a wide particle size distribution are major problems that led to the development of several alternative techniques to synthesize ceramic powders [4]. The oxidant peroxide method (OPM) is one of the most interesting wet-chemical routes for the synthesis of lead or bismuth based materials [5]. This route was named to as the oxidant peroxo method (OPM) and is based in the fundamental oxy-reduction reaction between lead (II) ions and several water-soluble titanium peroxo complexes.

This reaction results in an amorphous and reactive precipitate free of any common contaminants found in materials synthesized by other routes that use organic compounds to stabilize cations in solution [6–8]. Usually, residual carbon can be eliminated only after annealing at high temperatures, however it completely modifies the final properties and destroy the quality of powders synthesized by wet-chemical routes [9,10].

Although powders synthesized by the OPM route show evident advantages regarding purity, reactivity, particle size and size distribution, many of the final properties of fine ceramics are determined by the sintering procedure. Conventionally, PZT ceramics require high temperatures exceeding 1250 °C, which is undesirable due to lead volatilization and a consequent loss in the composition that adversely affects the piezoelectric properties [11]. There has been a growing interest in the heating and sintering of ceramics by microwave radiation [12]. Since the first study demonstrating that PZT can be successfully prepared by the OPM route [13], efforts have been directed toward obtaining dense ceramics [14]. Apart from the extensive data available for PZT, little is known about the use of microwaves. Recently, Raju and Reddy [15] reported the influence of microwave sintering on the structural and dielectric properties of lead zirconate titanate using very reactive powders synthesized by the citrate method with a composition around the MPB. Ramana et al. [16] compared microwave sintering with the conventional method using PZT powders synthesized by the solid state reaction and concluded that microwave

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radiation can improve the densification at lower temperatures and can also reduce the soaking time. In this process, heat is generated internally within the material instead of originating from external sources and is responsible for a unique microstructure and uniformity [17]. It should be noted that all these studies indicated that microwave sintering is a promising technique to obtain highly dense ceramics with superior dielectric behavior.

In this study, we are presenting the synthesis of lead zirconate titanate powders by the OPM route and the electrical characterization of dense ceramic bodies with composition near to the MPB region sintered by conventional and microwave processing, which resulted in ceramics with a maximum dielectric constant of 17.911 and an anomalous high Curie temperature of 465 °C.

2. Experimental

2.1. Synthesis and sintering

All chemical reagents were used as received. Three nominal compositions of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ($x=0.20, 0.48$ and 0.80 , with samples referred to as PZTX where "X" indicates the percentage of titanium) were prepared by the OPM route [5]. In a typical procedure, 1 g (0.02 mol) of titanium metal powder (99.7%, Aldrich, Germany) was added into a mixture of 80 mL of hydrogen peroxide (analytical grade, Synth, Brazil) and 20 mL of aqueous ammonia solution (analytical grade, Synth, Brazil). This solution was left in an ice-water bath for approximately 5 h, resulting in a yellow transparent aqueous solution of soluble peroxytitanate $[\text{Ti}(\text{OH})_3\text{O}_2]^-$ ions. Zirconyl (IV) nitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 99.99%, Aldrich, Germany) was previously submitted to gravimetric analysis by heat treatment at 900 °C for 2 h to estimate the exact molar quantity of zirconium per gram. The $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ was weighed and added into 100 mL of deionized water and lead nitrate (99.9%, Aldrich, Germany) was added to complete the desired stoichiometric molar ratio. Finally, the solution of zirconium and lead nitrates was slowly dripped into the peroxytitanate solution under stirring, resulting in a vigorous evolution of gas. The system lost its yellow color and an orange precipitate formed immediately exothermically. This precipitate was filtered and washed with diluted ammonia to eliminate nitrate ions. The washed amorphous precipitate was dried at 50 °C for 5 h and ground using a mortar. Amounts of 0.20 g of the amorphous powder were calcined between 400 and 900 °C for 2 h using a heating rate of 10 °C min^{-1} in closed alumina boats. Disks (10 mm diameter and 1.1 mm thick) were prepared with 0.50 g of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ powders calcined at 700 °C for 2 h and isostatically pressed with a load of 30 t for 1 min. After pressing, the disks were sintered at 1000 °C for 2 h using (i) a tubular oven with a heating rate of 10 °C min^{-1} and (ii) a microwave oven with heating rate of 25 °C min^{-1} . To avoid lead volatilization, samples were sintered using closed zirconia crucibles, keeping them immersed in a powder with the

same composition of the sample. The relative densities of sintered samples were measured using the Archimedes method.

2.2. Characterization

Amorphous precursors (10 mg) were analyzed by differential scanning calorimetry (Netzsch DSC 204 Phoenix) in the range from -100 to 550 °C at heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The amorphous precursor, heat-treated powders and all sintered samples were characterized at room temperature by Fourier transform Raman spectroscopy (FT-Raman, Bruker RFS 100/S) using the 1064 nm line of a yttrium aluminum garnet laser. These samples were also characterized by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (Rigaku D/MAX 200 with a rotary anode operating at 150 kV and 40 mA) in the 2θ range from 5° to 75° with a step scan of 0.02° . The specific area of PZT powder heat-treated at 700 °C for 2 h was determined by BET isotherms using a Micromeritics ASAP 2000. The powder morphology was verified by transmission electron microscopy (TEM, Philips CM200), and the cleaved sintered ceramics were characterized by high-resolution field emission scanning electron microscopy (FE-SEM, Zeiss Supra 35 at 2 kV). The fractured surface composition was determined by energy dispersive X-ray (EDX) spectroscopy (FEI XL30 FEG with an Oxford Instruments – Link ISIS 300 detector). For the electrical measurements, gold contacts were sputtered on two opposite faces of the disks, and the dielectric constant (ϵ') of the sintered samples was measured in the temperature range from 30 to 500 °C using a Keithley 3330 (LCZ) meter at different frequencies (1, 10, and 100 kHz). Two different heating rates were evaluated (1 and 5 °C min^{-1}) and the 1 °C min^{-1} was chosen to carry out to measure the dielectric constant. In order to guarantee the furnace temperature stability, each value of the dielectric constant was collected only after leaving the sample for 30 min in each temperature.

3. Results and discussion

Although PZT is widely investigated, there are only a few studies about PZT powders synthesized by the OPM route [5,13]. Despite this fact, it is well known that the amorphous precipitate is rich in peroxide groups that release a large amount of oxygen gas during their exothermic decomposition [5–8,13,14,18]. For this reason, sintered ceramics prepared directly from the amorphous precipitate are fragile. On the other hand, powders calcined at temperatures higher than the peroxide decomposition are highly reactive [5,8,14]. To find the best calcination temperature, we evaluated the PZT powders calcined at temperatures from 400 to 900 °C. Due to the high reactivity, powders calcined at higher temperatures revealed large agglomerates partially sintered. Powders calcined up to 600 °C were poorly crystalline and revealed a mixture of tetragonal and rhombohedral phases that

Table 1
Lattice parameters, tetragonality factor (c/a), and unit cell volume for $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ with $x=0.20; 0.48$ and 0.80 powders calcined at 700 to 900 °C for 2 h.

Composition	Geometry	Heat treatment (°C)	A=b (Å)	c(Å)	V(Å ³)	c/a	File JCPDS
PZT80	Tetragonal	900	3.9597 ± 0.0001	4.1314 ± 0.0001	64.776 ± 0.003	1.043	6–452
		800	3.9529 ± 0.0001	4.1347 ± 0.0001	64.606 ± 0.003	1.046	
		700	3.9354 ± 0.0001	4.1437 ± 0.0001	64.174 ± 0.003	1.053	
PZT48	Tetragonal	900	4.0473 ± 0.0002	4.1342 ± 0.0003	67.720 ± 0.007	1.021	50–346
		800	4.0193 ± 0.0002	4.1243 ± 0.0003	66.626 ± 0.008	1.026	
		700	4.0022 ± 0.0002	4.1057 ± 0.0003	65.762 ± 0.007	1.026	
PZT20	Rhombohedral	900	5.2529 ± 0.0003	13.912 ± 0.0013	332.45 ± 0.04	–	89–1276
		800	5.2541 ± 0.0003	13.909 ± 0.001	332.53 ± 0.04	–	
		700	5.2544 ± 0.0003	13.907 ± 0.001	332.52 ± 0.04	–	

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