Analysis of Ca-PZT powder obtained by the Pechini and partial oxalate methods

(Análise do pó de PZT-Ca obtido pelo método Pechini e método do oxalato parcial)

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Abstract

$Ca\text{-}Pb(Zr,Ti)O_3$ (Ca-PZT) powders were prepared by a combined method, Pechini technique for the intermediate $ZrTiO_4$ (ZT) particles and oxalate route for the final powder. The intermediate and final products were characterized by X-ray diffraction and BET for phase identification and granulometric analysis, respectively. The surface area of ZT powder reduced remarkably from 70 to 7.4 m^2/g when the calcining temperature increased from 600 to 800 °C. Incremental pore volume and average pore diameters of the powder calcined at 700 °C for 3 h were 0.026 cm^3/g and 70 Å, respectively. Ca-PZT powder calcined at 800 ºC for 3 h, with agglomeration factor (AF) 2.8, showed no hysteresis in BET analysis, which indicate small agglomeration without micropores among particles. The powder calcined at 750 ºC for 3 h, however, exhibited small AF and high sinterability.
Keywords: Pechini method, Ca-PZT, powder sintering.

Resumo

Pós de $Ca\text{-}Pb(Zr,Ti)O_3$ (Ca-PZT) foram preparados por um método combinado que consiste na técnica Pechini para as partículas intermediárias de $ZrTiO_4$ (ZT) e a rota do oxalato para o pó final. Os produtos intermediário e final foram caracterizados por difração de raios X e determinação de área de superfície específica pelo método BET, respectivamente. A área de superfície específica do pó de ZT reduz bastante de 70 para 7,4 m^2/g com o aumento da temperatura de calcinação de 600 para 800 °C. O volume incremental de poros e os diâmetros médios de poros do pós calcinado a 700 °C / 3 h forma 0,026 cm^3/g 4 70 Å, respectivamente. O pós de Ca-PZT calcinado a 800 °C / 3 h, com fator de aglomeração 2,8, não apresentou histerese na análise de BET, o que indica pequea aglomeração sem micriporos entre as partículas. O pó calcinado a 750 °C / 3 h, contudo, apresentou pequeno fator de aglomeração e alta sinterabilidade.
***Palavras-chave**: método Pechini, Ca-PZT, sinterização de pós.*

INTRODUCTION

Several synthesis methodologies [1-3] of lead zirconate titanate, $Pb(Zr,Ti)O_3$ - PZT were used to obtain high phase homogeneity, high surface area and a small level of powder agglomeration which lead to dense bodies and materials with high piezoelectric properties after sintering [4, 5]. The chemical synthesis, such as co-precipitation [6], sol-gel [7] and others [8] could cause high agglomeration of precipitate powder or small size particles (> 50 nm) that lead to a decrease in the powder sinterability.

An advantage of the Pechini method [9] is the nucleation of an amorphous powder with diameter of a few nanometers allowing growth and phases crystallization control.

Recent work [10, 11] used $ZrTiO_4$ (ZT) as an intermediary phase in the PZT synthesis. High temperatures for the ZT phase formation [12] leads to the use of a chemical synthesis method that promotes decrease of temperature during the phase formation. As an example $Zr_xTi_{1-x}O_4$ at composition ranges among $0.35 \leq x \leq 0.65$ was synthesized using the Pechini method with high phase homogeneity and small particle size distribution [13]. Different methods were used for the ZT phase synthesis, such as combination of the spray decomposition method with solid state reaction [14] and partial oxalate (PbO) with hydrothermal reaction (ZT) [15].

Compositional fluctuation in PZT near the morphotropic phase boundary (MPB) [16, 17] region is caused by Ti and Zr ions migration due to microregions of different chemical potentials. Non-stoichiometric conditions could occur due to high loss of PbO [18] during calcination and sintering stages. PbO loss during the calcination and sintering stages [19, 20] of the PLZT phase leads to the use of a synthesis process

that causes a minimum evaporation effect. Thus, a diffusion process by interfaces decreases the PbO volatilization during the heating stages. The PbO phase obtained by partial oxalate method with decomposition onto the ZT particles decreases such effect due to the diffusion process that occur at low temperatures. PbC_2O_4 was decomposed on ZT surface particles to obtain niobium doped lead zirconate titanate, PZTN at 650 °C/6 h [15]. Densities close to the theoretical values were obtained after sintering. Different precipitation routes were used [21] and grain sizes close to 2.0 μm were obtained by sintering at 1200 °C/2.5 h. PLZT was sinthesized by precipitation of PbC_2O_4 on ZT particles to obtain a calcined powder with 2.2 μm of diameter [11].

Small significance has been done for substitutions of calcium in PZT due to a strong powder agglomeration tendency that degrades all properties of the sintered material. Synthesis by precipitation of calcium in PZT [22] shows powders with strong agglomeration level. Agglomeration with low surface area caused a degradation of the ferroelectric and piezoelectric properties. Pb partially replaced by Ca or Sr [23] shows better properties than the PZT with 1 mol % of calcium substitutions.

The purpose of the present work is to synthesize and analyze the powder characteristics of Ca-PZT using two processing methods: the Pechini for ZT and the partial oxalate for Ca-PZT.

EXPERIMENTAL

High purity raw materials, zirconium IV propoxide, titanium IV isopropoxide, $Pb(NO_3)_2.6H_2O$ and $Ca(NO_3)_2.5H_2O$ were used for the synthesis of $Pb_{0.95}Ca_{0.05}(Zr_{0.53}Ti_{0.47})O_3$ solid solutions.

ZT synthesis by the Pechini method

Stoichiometric mixture of titanium IV isopropoxide, zirconium IV propoxide in citric acid and water (80/20 vol.%) were prepared at 90 °C at concentrations of 7.4% TiO_2 of Ti citrate solution and 7.1% ZrO_2 of Zr citrate solution. A mixture of resins with a stoichiometry of 0.47 mol % of TiO_2 and 0.53 mol % of ZrO_2 was prepared at 100 °C. After homogenization, ethylene glycol was added at a mass ratio of 40/60 relative to the citric acid. A rigid polymeric resin obtained at 250 °C / 2 h was decomposed and ground in a ball mill, calcined for 3 h at different temperatures and characterized by XRD and BET.

Ca-PZT synthesis by the partial oxalate method

The ZT particles were dispersed in water under stirring. Stoichiometric amount of lead nitrate (0.995 mol %) and calcium nitrate (0.005 mol %) were dissolved in the solution. A precipitation of PbC_2O_4 and CaC_2O_4 on the ZT surface occurs by addition of NH_4OH. The precipitated product was washed, filtered and dried in an oven at 70 °C. The powder was ground, sieved at 325 mesh, calcined in the temperature range 350-800 °C for 3 h and characterized by XRD and BET.

RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns of the ZT (53/47) powder calcined from 350 °C to 700 °C/3 h with intense peaks of the crystalline phase at 700 °C. During the decomposition of the polymeric resin of citrates, an increase of the ZT crystalline phase up to 600 °C is observed. Comparison among processes, such as solid-state reaction [1], precipitation [2] and others [3] demonstrated that high temperature is necessary for the ZT phase formation. The ZT phase was synthesized using a polymeric precursor method observing high crystallinity close to 700 °C [5, 21].

Surface area of the ZT crystalline powder was remarkably reduced from 70 to 7.4 m^2/g with 600, 700 and 800 ºC calcination temperatures. The particle growth occurs when an increase of intensity of the $2\theta = 37º$ peak is observed.

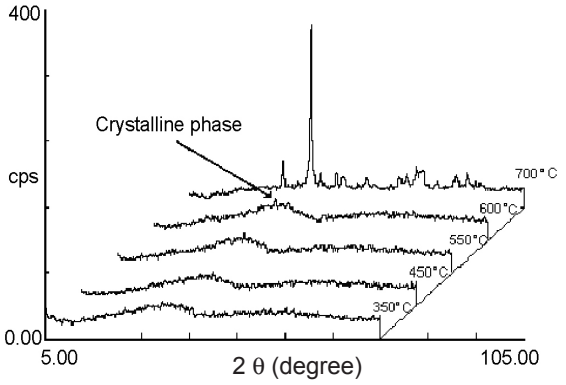

Figure 1: X-ray diffraction pattern of the ZT (53/47) phase.
[Figura 1: Difração de raios X da fase ZT (53/47).]

Fig. 2 shows the characteristic curves of adsorption/ desorption of ZT powders calcined at 600 and 700 ºC with a hysteresis formation. A hysteresis H type II (bottle shape) and isotherm IV type at 600 °C indicated that microporosity

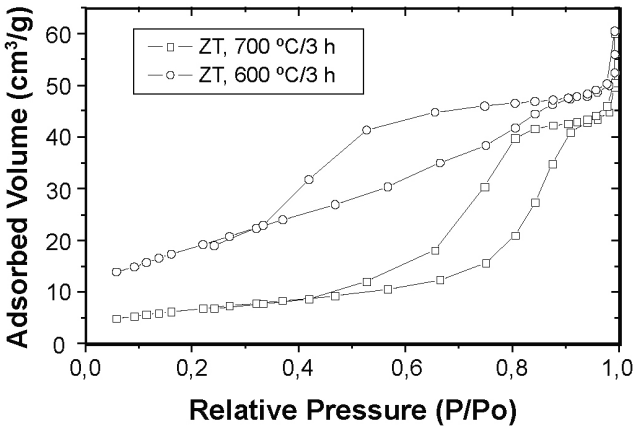

Figure 2: Adsorbed volume versus relative pressure of the ZT phase. **Powder calcined at 600 and 700 ºC/ 3 h.**
*[Figura 2: Volume adsorvido em função da pressão relativa da fase ZT. **Pó calcinado a 600 e 700** °C/3 h.]*

(r < 2 nm) does not occur. At 700 °C a hysteresis H I type (cylindrical shape) and isotherm IV type was observed indicating open porosity.

Fig. 3 shows the incremental pore volume of the ZT powder calcined from 600 °C to 700 °C demonstrating a change of the average pore diameter from 35 Å (at 600 °C) to 55 Å (at 700 °C) (mesopores) caused by an increase of the particle size with an increase of the pore volume. Volume adsorption of about 0.030 cm^3/g indicated that a small agglomeration of nanoparticles took place.

Characterization of the Ca-PZT powders

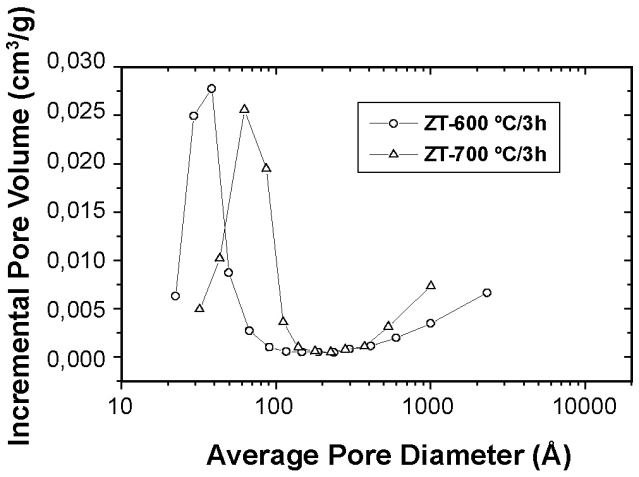

Figure 3: Incremental pore volume versus average pore diameter of the ZT phase.
[Figura 3: Volume incremental de poros em função do diâmetro de poros da fase ZT.]

Fig. 4 shows the X-ray diffraction pattern of a monophasic solid solution of the Ca-PZT phase with tetragonal structure. According to several authors [6, 7] the compositional fluctuation of Zr and Ti ions occurs near the Zr concentrations between 50 and 53 mol% in the phase diagram of PZT. Such range of the Zr concentrations caused a coexistence between a F_T (ferroelectric tetragonal) and F_R (ferroelectric rhombohedral) phase inside the MPB (morphotropic phase boundary). Calcium additions in PZT diminished the compositional fluctuation and dislocated from the MPB to F_T phase (Zr rich region).

An internal interface ZT/Ca-PZT/PbC_2O_4-CaC_2O_4 was formed and a high surface area reduction from 25 m^2/g (ZT phase) to 2 m^2/g (Ca-PZT phase) at 600 °C/3 h occurred.

Comparisons between particle sizes of the Ca-PZT phase using BET and XRD methods are shown in Table I, with an agglomeration factor ($AF=D_{BET}/D_{XRD}$) of 1.7 at 700 °C/3 h and 2.8 at 800 °C/3 h. The analysis shows that gas adsorption with two and three particles occurs, respectively, and demonstrate that the BET analysis data presents larger particle size compared with the crystallite size obtained by XRD. A small agglomeration of powder could be accepted considering that the XRD analysis shows a primary particle diameter in a specific crystalline direction.

Table I - Surface area, average particle size by BET and average particle size by XRD of calcined Ca-PZT powder.
[Tabela I - Área de superfície específica, tamanho médio de partícula por BET e por difração de raios X de pós de Ca-PZT.]

	600 ºC	*650 ºC*	*700 ºC*	*750 ºC*	*800 ºC*
A_{BET} (m^2/g)	3.20	2.95	2.42	2.28	1.08
D_{BET} (nm)	235.80	255.60	312.50	331.00	698.00
D_{XRD} (nm)	63.92	72.25	181.80	229.00	252.60

Fig. 5 shows a hypothetical mechanism of the Ca-PZT phase formation consisting of a decomposition of PbC_2O_4 - CaC_2O_4 with formation of PbO and CaO onto the ZT particle (surfaces of the particles). Pb and Ca ions migrate towards the ZT phase and the Ca-PZT phase is formed between two different phases (ZT and PbO-CaO). Constant diffusion of Pb and Ca ions across the Ca-PZT phase occurs and growth, such as towards the ZT phase as well as in the direction of PbO-CaO phases .

Fig. 6 shows a hysteresis curve of H2 type and isotherm

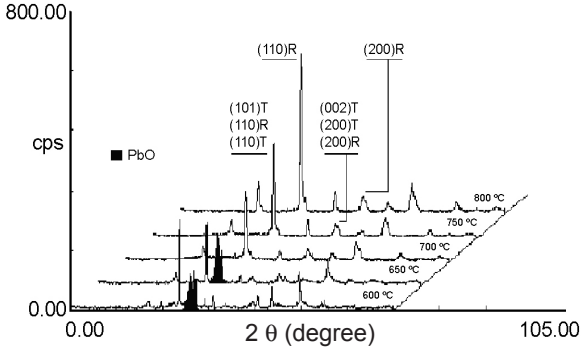

Figure 4: X- ray diffraction pattern of the Ca-PZT phase.
[Figura 4: Difração de raios X da fase Ca-PZT.]

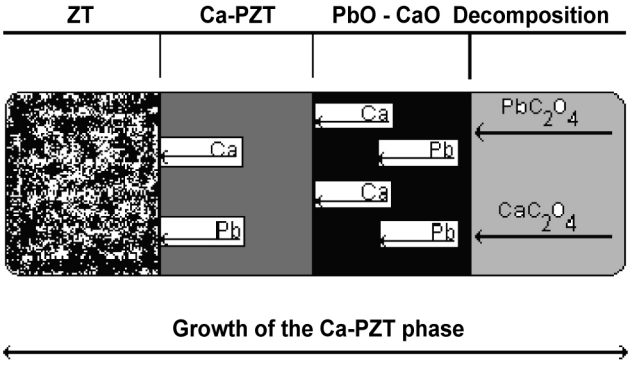

Figure 5: Mechanism of the Ca-PZT phase formation.
[Figura 5: Mecanisno da formação da fase Ca-PZT.]

curve of type II (bottle shape pores) at 600 °C/3 h. Such characteristics demonstrate that an agglomeration between particles may be present and it is in agreement with the AF calculations. At 800 °C/3 h an isotherm curve type II is observed and a small hysteresis behavior occurs. Such fact demonstrates that a large quantity of agglomerated particles reacts by a diffusion process, decreases the porosity and forms large particles.

Fig. 7 shows the incremental pore volume at 600 ºC/3 h

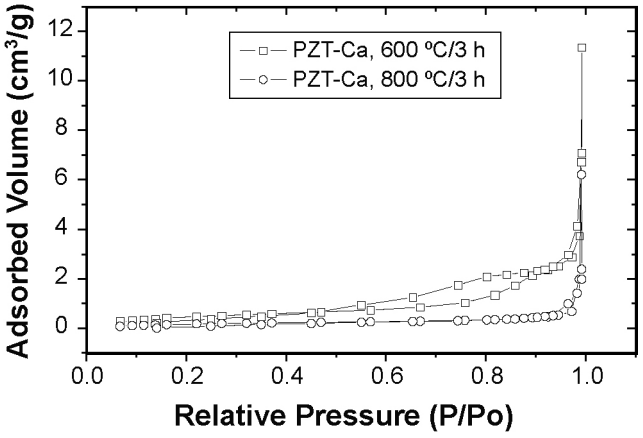

Figure 6: Adsorbed volume versus relative pressure of Ca-PZT phase. Powder calcined at 600 and 800 ºC/3 h.
[Figura 6: Volume adsorvido em função da pressão relativa da fase Ca-PZT. Pó calcinado a 600 e 800 °C/3 h.]

indicating that the presence of mesopores (30-100 Å), indicating a rapid increase of porosity at 300 Å characterizing macropores. Similar analysis of the powder at 800 °C/3 h shows a rapid increase of pore volume above 300 Å indicating growth of macroparticles (clusters) and shows a large increase of pore volume. However, particles (clusters) with small agglomeration level were densified and suppressed a residual porosity.

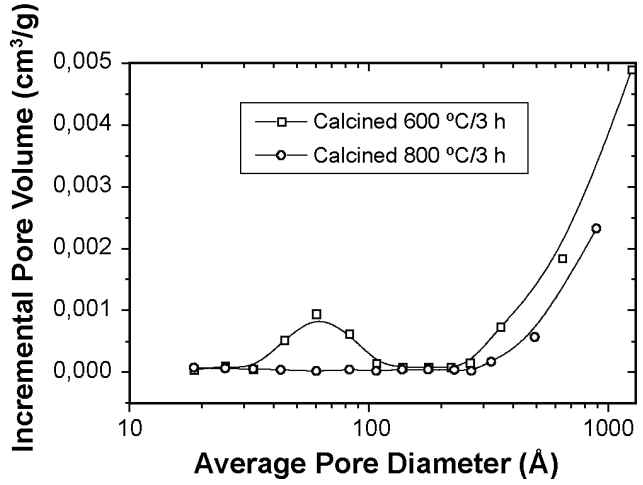

Figure 7: Incremental pore volume versus average pore diameter of the Ca-PZT phase. Powder calcined at 600 and 800 ºC/3 h.
[Figura 7: Volume incremental de poro em função do diâmetro do poro da fase Ca-PZT. Pós calcinado a 600 e 800 °C/3 h.]

Fig. 8 shows a kinetic analysis of particle growth of the Ca-PZT phase. The straight lines show a change of slope above 700 °C indicating that a change of mass transport occurs. Below 700 °C a contact between particles of the powder due to agglomeration caused neck formation characterized by a non densifying mass transport mechanism, such as a surface diffusion process. A strong reduction of surface area by grain boundary diffusion or volume diffusion mechanisms is possible to occur.

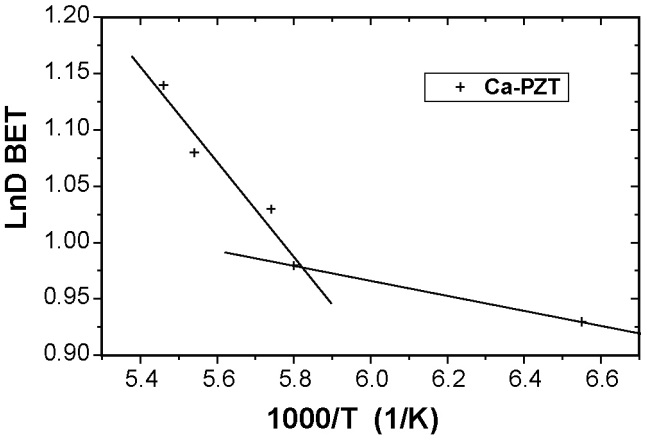

Figure 8: Dependence of the BET particle size on the teciprocal of the absolute calcination temperature of Ca-PZT powder.
[Figura 8: Dependência do tamanho de partícula da fase Ca-PZT determinada por BET com o recíproco da temperatura absoluta de calcinação.]

CONCLUSIONS

The synthesis of the Ca-PZT powder by the Pechini and the partial oxalate methods promoted small agglomeration of powder for both ZT and Ca-PZT synthesis. Analysis by BET of the ZT phase shows high reduction of surface area from 70 m^2/g at 600 °C/3 h to 24.6 m^2/g at 700 °C/3 h. Ca-PZT calcined at 700 °C/3 h shows surface area 2.42 m^2/g. Agglomeration factor of 1.8 at 700 °C/3 h and 2.8 at 800 °C/3 h were determined. Hysteresis behavior indicated that agglomeration of powder occurs and the porosity increases with an increase of the particle size of Ca-PZT. The incremental pore volume shows the presence of mesopores (30-100 Å) and macropores (300 Å) indicating particle growth during calcination.

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