Thermal Analysis of PT Ceramics Obtained by Sol-Gel Processing

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$PbTiO_3$ (PT) ceramics are prepared by sol-gel method, utilising as precursors Titanium (IV) isopropoxide $Ti[OCH(CH_3)_2]_4$, 99.99% purity and Lead (II) acetate trihydrate $Pb(CH_3COO)_2 \cdot 3H_2O$, 99% purity, and 2-methoxyethanol $CH_3OCH_2CH_2OH$ as solvent. Thermal analysis was performed in the temperature range 400ºC up to 500ºC, with 5ºC/min rate. Crystallised ceramics present high transition temperatures, high Curie points and thermal hysteresis, closed to 490 ^{0}C. Crystallisation and morphology properties are investigated by SEM, and DSC analysis. SEM micrographs analysis proves crystallisation structure for the PT powders.

1. Introduction

Lead titanate $PbTiO_3$ (PT), which exhibits a perovskite structure and a Curie temperature of 490 ^{0}C, belongs to the most important ferroelectric and piezoelectric families. The sol-gel method advantages of Lead titanate $PbTiO_3$ processing are the mixing of reactants on a molecular level, a better control of stoichiometry, higher purity raw materials, and the easy formation of ultrafine and crystallized powders [1]. The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxides [2]. The sol-gel method applies to porous materials, dense materials like glasses and ceramics, organic-inorganic hybrids and nanocomposites [3]. It was found that a possible improvement of the crystallization process is to use power ultrasound [4].

2. Experimental sol-gel method for $PbTiO_3$ ceramics

$PbTiO_3$ (PT) ceramics are prepared by sol-gel method, utilising as precursors Titanium (IV) isopropoxide $Ti[OCH(CH_3)_2]_4$, 99.99% purity and Lead(II) acetate trihydrate $Pb(CH_3COO)_2 \cdot 3H_2O$, 99% purity, and 2-metoxietanol $CH_3OCH_2CH_2OH$ as solvent. The gel is prepared by addition of equal volumes of precursor solution (sol) and a solution, containing water (Rw = 2.5) and 2-metoxietanol as solvent. In the preliminary gel drying process, the gel is heated at 200 ^{0}C for 12 hours. After that, the amorphous powder is heated at 300 ^{0}C for 24 hours. Secondarily, the drying process is made at 500 ^{0}C for 2 hours. The amorphous powder is crystallised at 800 ^{0}C for 2 hours, and cooled in air.

Two $PbTiO_3$ samples are obtained, namely A and C (ultrasound gel). Before the drying process the gel was ultrasound irradiated. Ultrasonic vibrations propagated through the gel and induced cavitation effects. To obtain C sample, after gel ultrasound irradiation the preliminary drying of gel was performed at 200 ^{0}C, during one hour, instead of 12 hours that in the case of A sample. The crystallisation and morphology properties of ceramic powders are investigated by DSC analysis. The thermal properties were obtained in the temperature range 400ºC up to 500ºC, with a rate of 5ºC/min. Figure 1 presents the heat flux function of temperature curves, for A and C samples. Figure 2 presents the heat flux curves function of time for A and C samples, at 5ºC/min temperature rate. The SEM micrograph presented in

Figure 4 shows the grater size grains for C sample, comparatively with the grains of A sample (Figure 3).

3. Conclusions and discussions

Crystallization preparation by a thermal process of dense crystalline ceramics depends on the process duration. Also, the temperature conditions have influence in the size increasing of the crystal grains. The study of the crystallization upon heating was performed using the technique differential scanning calorimetry (DSC). Thermal curves were determined in the temperature range 400ºC up to 500ºC, with a rate of 5ºC/min. The two $PbTiO_3$ powders have also been comparatively studied in thermal analysis and particle morphology. It has been observed that the crystalline structure of PT powder type C has been modified by ultrasound irradiation. Ultrasound irradiation implies a better nucleation, and has influence on the growth rate and the crystals size distribution. Both PT crystallised ceramics present high transition temperatures, high Curie points closed to 490 ^{0}C and thermal hysteresis.

References:

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Figures:

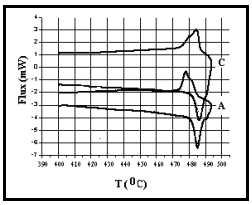

Fig. 1 Heat flux curves function of temperature for A and C samples, at 5ºC/min temperature rate

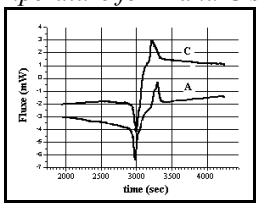

Fig. 2 Heat flux curves function of time for A and C samples, at 5ºC/min temperature rate

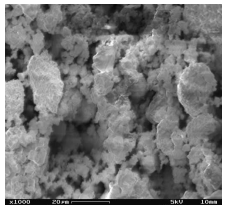

Fig.3 SEM microstructure of PT sol-gel powder (A sample)

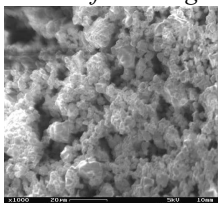

Fig.4 SEM microstructure of PT sol-gel powder (C sample)