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HYSTERESIS ANALYSIS OF $PBTiO_3$/P(VDF-TrFE) 0-3 COMPOSITES

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Rezumat. *Lucrarea studiază pulberile de titanat de plumb* ($PbTiO_3$) *în forma tetragonală, care au fost preparate cu succes prin metoda sol-gel. Producerea ceramicilor de titanat de plumb* PT *a fost urmata de difracţia de raze X (XRD) şi microscopie (SEM). Pulberile de titanat de plumb au fost obţinute în diferite condiţii, funcţie de temperatura de ardere şi de câmpul ultrasonic. Compozitele* $PbTiO_3$/P(VDF-TrFE) *au fost realizate sub forma* 0-3 *pulbere* PT *si polimer* P(VDF-TrFE *au fost polarizate in ulei siliconic la* 100 ^oC. *Analiza histerezisului a fost examinată experimental. Astfel în condiţiile procesului sol-gel al pulberii, se poate înţelege mai bine corespondenta intre proprietăţile pulberii şi compozitele* 0-3, *în funcţie de tratamentul termic.*

Abstract. *Lead titanate (*$PbTiO_3$) *powders in tetragonal form have been successfully prepared by sol-gel method. The processing of lead titanate* PT *ceramics was followed up using X-ray diffraction (XRD), and microscopy (SEM). Lead titanate powders have been obtained in different conditions function of annealing temperature and ultrasound field.* $PbTiO_3$/P(VDF-TrFE) 0-3 *composites made by the PT powders and P(VDF-TrFE) polymer were polarized in silicon oil at* 100 ^oC. *The hysteresis analysis has been investigated experimentally. Therefore, one can better understanding the correspondence between the powder properties and the 0-3 composites, function of thermal treatment conditions of sol-gel processing powders.*

Keywords: hysteresis, $PbTiO_3$, P(VDF-TrFE), $PbTiO_3$/P(VDF-TrFE) 0-3 composite

1. Introduction

$PbTiO_3$ (PT) ceramics were prepared by sol-gel method, utilizing 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 $CH_3OCH_2CH_2OH$, 2-metoxi-etanol as solvent. Lead titanate ceramics type $PbTiO_3$, which exhibits a perovskite structure and high Curie temperature of 490 ^0C belong to the most important ferroelectric and piezoelectric families. Some of the advantages of sol-gel method are the mixing of reactants on a molecular level, a better control of stoichiometry, higher purity raw materials, and easy formation of ultra-fine and crystallized powders [1]. Ferroelectric ceramics, as lead titanate (PT) show a high electromechanical coupling coefficient, k_t, a large range of dielectric constant

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values and low dielectric and mechanical losses. However, these ceramics have high acoustic impedance and low flexibility [2].

The preparation of the ceramic powders by sol-gel technique allows one to obtain pure ceramic powders with controlled morphology and gain size [3]. In the sol-gel process the precursors for preparation colloid consists of a metal or metalloid element surrounded by various ligands. Metal alkoxides are popular precursors because they react readily with water. The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the metal atom. Two partially hydrolyzed molecules can link together in a condensation reaction. Condensation liberates a small molecule, such as water. A gel is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. The continuity of the solid structure gives elasticity to the gel. Gelation can be produce by rapid evaporation of solvent, as occurs during preparation of films or fibers. Gelation can occur after a sol is cast into a mould, in which case it is possible to make objects of desired shape. Aging of gel may involve further condensation, dissolution and reprecipitation of monomers, or phase transformation within the solid or liquid phases. Drying by evaporation under normal conditions gives rise to capillary, pressure that causes shrinkage of gel network. Most gels are amorphous, even after drying, but many crystallize when heated. Once a gel has been densified, it is equivalent to a ceramic made by conventional. After gel has been melted, however, it “forgets” its manner of preparation and acquires the equilibrium structure dictated by thermodynamics [4].

2. Experimental sol-gel method for $PbTiO_3$ ceramic powders

Two type of $PbTiO_3$/P(VDF-TrFE) 0-3 composites were manufactured by hot pressing of B-$PbTiO_3$ and D-$PbTiO_3$ and P(VDF-TrFE) powders, 50% volume fraction [5]. After that, composite thin films were polarized in silicon oil at 100 ^oC at high voltage around 15 KV/mm electrical field. The experimental data enabled to rise the hysteresis curves for $PbTiO_3$/P(VDF-TrFE) composites, corresponding to the total current and polarisation. The gel was prepared by addition of equal volumes of precursor solution (sol) and a solution, containing water (Rw = 2.5) and 2-metoxietanol as solvent (Figure 2). So, the jellification of solutions was controlled through a hydrolytic polycondensation, by water adding. In the drying process, the densification and removal of volatile compounds induce some modifications into the gel structure, solvent removal leads to microporosity and therefore the area surface increases. Gel conversion into amorphous powder through a thermal process is presented in Figure 3. During this process hydroxyl groups and some organic residuals are exothermic removed and induce appropriate mass decrease. Thereby, the water removal and burning of residual compounds, network collapses while the structure relaxes, and viscous sintering continues until the porous phase is eliminated. Densification of the amorphous gels by a thermal process implies structure relaxation, polymer condensation and viscous sintering. In the preliminary drying gel process, the gel is heated at 200 ^{0}C for 12 hours into a glass bottle, which is put into a silicon oil bath, and all this time it is rotated by a spinner. After that, the amorphous powder was heated into an oven at 300 ^{0}C for 24 hours. Secondarily, the drying process was made into an oven at 500 ^{0}C for 2 hours, and we obtained an amorphous powder. After that, the amorphous powder was crystallized into an oven at 800 ^{0}C for 2 hours, through out from oven and cooled in air [3]. Crystallization preparation by a thermal process of dense crystalline ceramics depends on the process duration. Also, the temperature conditions have influence in the increasing of the crystal grain size. Two kinds of $PbTiO_3$ samples, named B and D were obtained by sol-gel method, in different conditions, such as, B1 sample B.

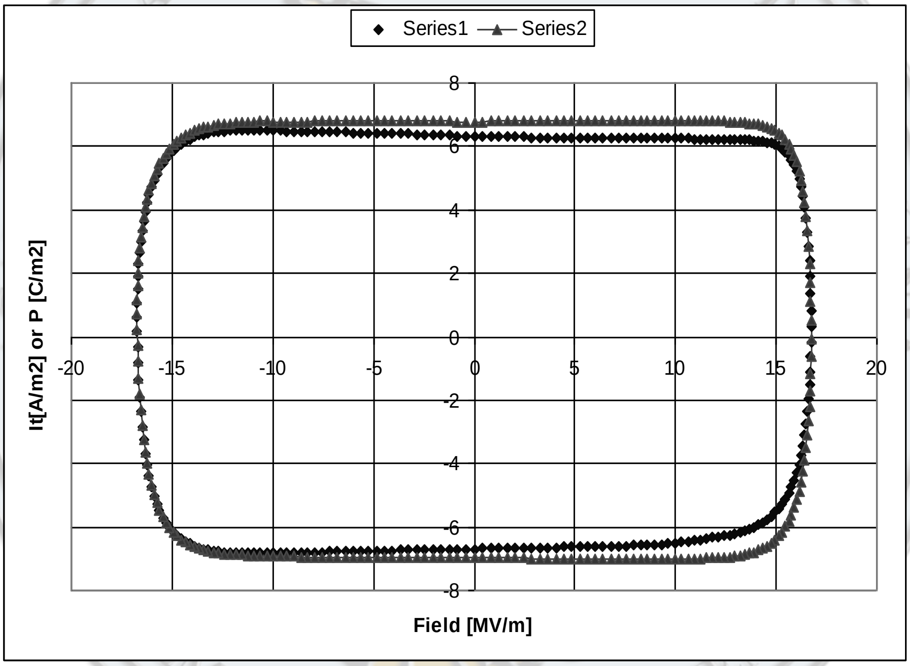

Fig. 1. Hysteresis curves for D1-$PbTiO_3$/P(VDF-TrFE) composite (series 1– current; series 2 - polarization)

By utilizing the previous described sol-gel process we realized powder sample, namely type B. In order to study the effects in the structure and morphology powders, at ultrasound irradiation, we made a transformation in the previous presented process. Our objective was to decrease the entire process duration, without damaging the final properties of the ceramic powder.

3. Results ceramic/polymer composites

Both hysteresis curves for D1-$PbTiO_3$/P(VDF-TrFE) composites were presented by series 1– current, and series 2 - polarization) (Fig. 1 and 2).

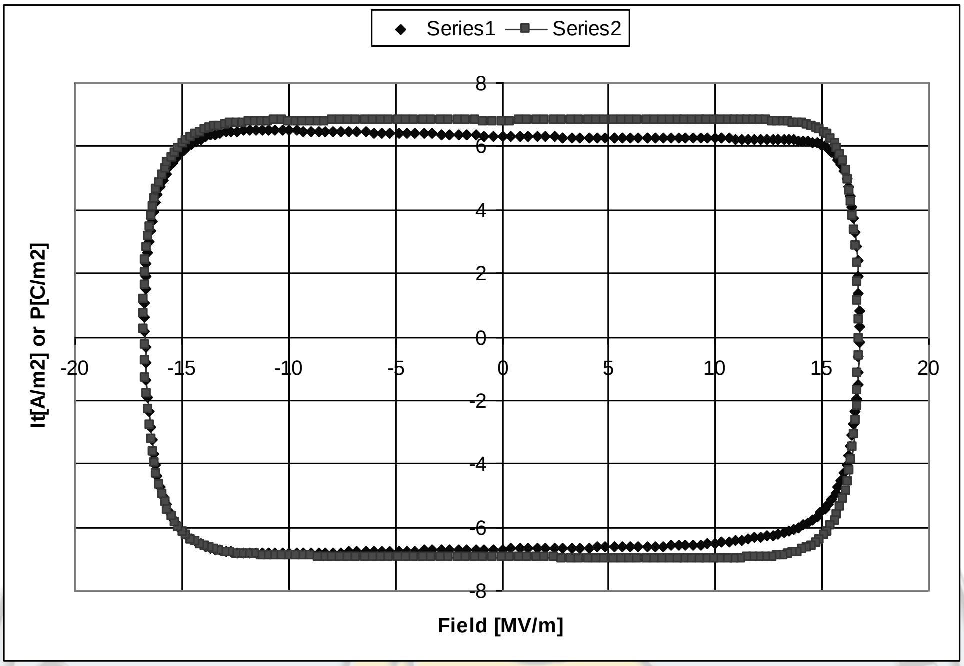

Fig. 2. Hysteresis curves for B1-$PbTiO_3$/P(VDF-TrFE) composite (series 1 – current; series 2 - polarization), where, I_t is total current [A/m^2] and P is Polarization [C/m^2]

Conclusions

Both ceramic / polymer composites (B1 and D1) yielded high coercitive fields and hysteresis forms. Indeed they could be appropriate utilized in digital systems.

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