Preparation of PbTiO$_3$ by seeding-assisted chemical sol-gel

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Abstract

Lead Titanate has been prepared by a sol-gel method using titanium tetrabutoxide and lead acetate in stoichiometric proportion. It was found that the seeding with solid PbTiO$_3$ nanometer-size particles (5 and 10 wt%) into the precursor solution plays a crucial role during crystallisation. At 380° and 400°C, the fraction of crystallisation of the PbTiO$_3$ perovskite phase for seeded sample is much higher than that corresponding to the unseeded one. Unseeded gel remained almost amorphous at 400°C, whereas the 5 and 10 wt% seeded gel was ≈50 and 85% crystalline. Besides, while unseeded calcined gels exhibit clearly the presence of pyrochlore phase at 425°C, this phase was not detected for the 5 wt% calcined seeded gel. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Lead Titanate, PbTiO$_3$, with a tetragonal perovskite structure at room temperature, is a ferroelectric compound with Curie Temperature of 490°C, high pyroelectric coefficients, high spontaneous polarization, low dielectric constant and low ageing rate of the dielectric constant [1]. Therefore, PbTiO$_3$ is useful as pyroelectric and piezoelectric base material for

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high temperature or high-frequency applications as nonvolatile memories, infrared sensors, microactuators, capacitors, and eletrooptic devices [2].

The sol-gel chemical processing has been extensively applied for preparing $PbTiO_3$. This method is mainly based on the hydrolysis of the complex alkoxide containing Pb-O-Ti units obtained by the reaction of the lead acetate and titanium alkoxide in 2-methoxyethanol [3]. Properties of these ceramics are strongly related to the stoichiometry. The presence of pyrochlore, a metastable intermediate phase, and/or lead-deficient secondary phases, $PbTi_3O_7$, caused by the loss of lead during thermal treatment, can damage significantly the electrical properties. Calzada et al. [4] reported that the formation of lead deficient phases delay and even hinder the formation of perovskite. Therefore the incorporation of an excess of PbO (20 mol%) to compensate the lead losses produced during heating, is necessary for obtaining the single perovskite phase without other crystalline structures. However, an excess of lead oxide can difficult the microstructures control. Kim et al. [5] reported a very important result, crack-free, undoped $PbTiO_3$ ceramics were prepared via sol-gel without excess of lead.

Seeding of Lead-derives Titanates have been studied previously. Zaghete et al. [6] reported the formation of PZT at 360°C for the material seeded with 5% of seed particles, approximately 400°C less than that formed by solid state reaction. Similarly, the influences of seeds and dopants on the perovskite and pyrochlore phase formation of PMN prepared by organic solution of citrates have also been studied [7]. Given that, the purpose of this work is the applying of the "seeding fundamental concepts" [8] to the preparation of $PbTiO_3$ by sol-gel using stoichiometric amounts of titanium and lead.

2. Experimental procedure

The preparation process is based on that proposed by V. Kumar [9]. In this case, $PbTiO_3$ precursor has been prepared by dissolving in stoichiometric proportion lead acetate in glacial acetic acid (1M) and titanium tetrabutoxide in isopropanol, 1/1 in volume. Both solutions were mixed at room temperature under constant stirring during 24 hour to ensure the formation of the intermediate precursor phase based on Pb-O-Ti bonding. Longer reaction times for the complex alkoxide synthesis larger polymerisation degree, tending to increase the perovskite phase formation at lower temperature [1]. For the hydrolysis of the precursor solution, a water-isopropanol mixture was slowly added maintaining the agitation. After this, fully crystalline $PbTiO_3$ seed particles were suspended in pure isopropanol and added to the transparent sol in a concentration of 5 and 10 percent of the total weigh. These $PbTiO_3$ seeds were previously prepared by this same method from an unseeded gel heated at 550°C. The crystal size of the seeds was ≈50nm, as was determined from the TEM analysis, Figure 1. To ensure a homogeneous dispersion of the $PbTiO_3$ seeds into the $PbTiO_3$ precursors sol, the agitation was maintained until the viscosity of the hydrolysed sol was enough to avoid the deposition of seeds. Then, the gel was deposited on a cristallisator and dried the gel at 60°C for 72 h. Dried gel monoliths were calcined at 380, 400 and 425°C, at 1°C/min of heating rate.

The crystallisation temperatures were determined by DTA/TGA (Netzsch STA-409) and
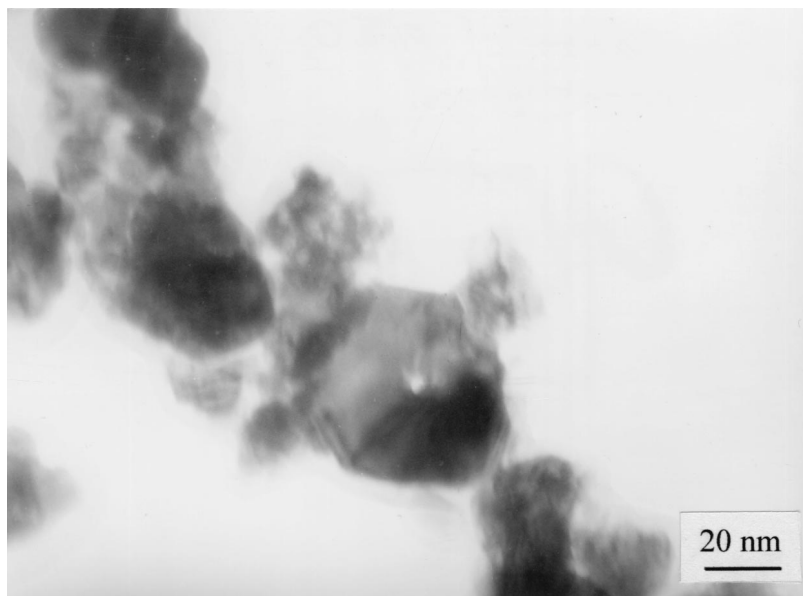
Fig. 1. TEM micrograph of PbTiO$_3$ seeds heated at 550°C.

the phase composition of calcining samples and the grade of cristallisation by XRD (Siemens D 5000). Powder morphology was observed by Transmission Electron Microscopy (Hitachi H 7000).

3. Experimental results

DTA and TGA curves of unseeded and 5, 10 wt% seeded samples heated from 25°C to 600°C in air are shown in Figure 2. First, a weight loss of about 27% appears at temperatures around 240°C, and this is associated with the main exothermic peak and corresponds to the combustion of the majority of the organic volatiles. Around 490°C, unseeded gel showed two small exothermic peaks, (482° and 500°C), by contrary the 5 and 10 wt% seeded samples showed just one small exothermic peak at ≈475°C. Those peaks can be attributed to the phase transformation to the crystalline perovskite phase, PbTiO$_3$ [10].

XRD analysis of unseeded and seeded samples calcined at temperatures of 380°, 400° and 425°C, see Figure 3, showed significative differences relative to the fraction of PbTiO$_3$ crystallisation and the pyrochlore phase formation. It can be clearly observed that the fraction of crystallised PbTiO$_3$ perovskite phase for seeded sample is much higher than that corresponding to the unseeded one. In this way, at 380°C unseeded gel remained almost amorphous up to 40 hours whereas 10 wt% seeded gel was >70% crystallised. At 400°C for 20 h, the unseeded sample showed about 20% crystallisation. The 5 and 10 wt% seeded samples, under the same conditions were 50 and 85% crystallised, respectively. In addition, 10 wt% seeded gel did not exhibit traces of pyrochlore. At 425°C for 10h., the pyrochlore phase was clearly observed in the unseeded calcined gels. By contrary, such a phase was not detected
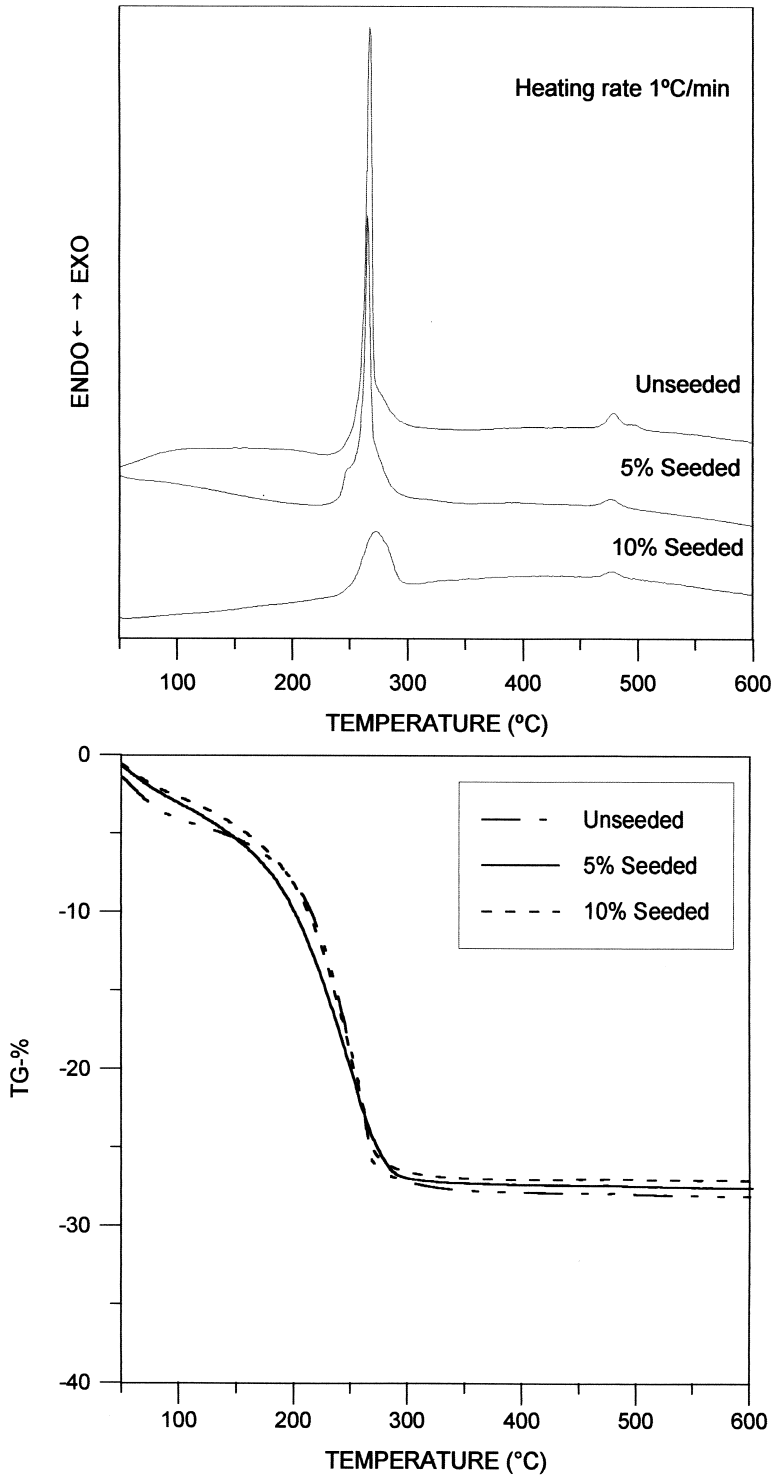
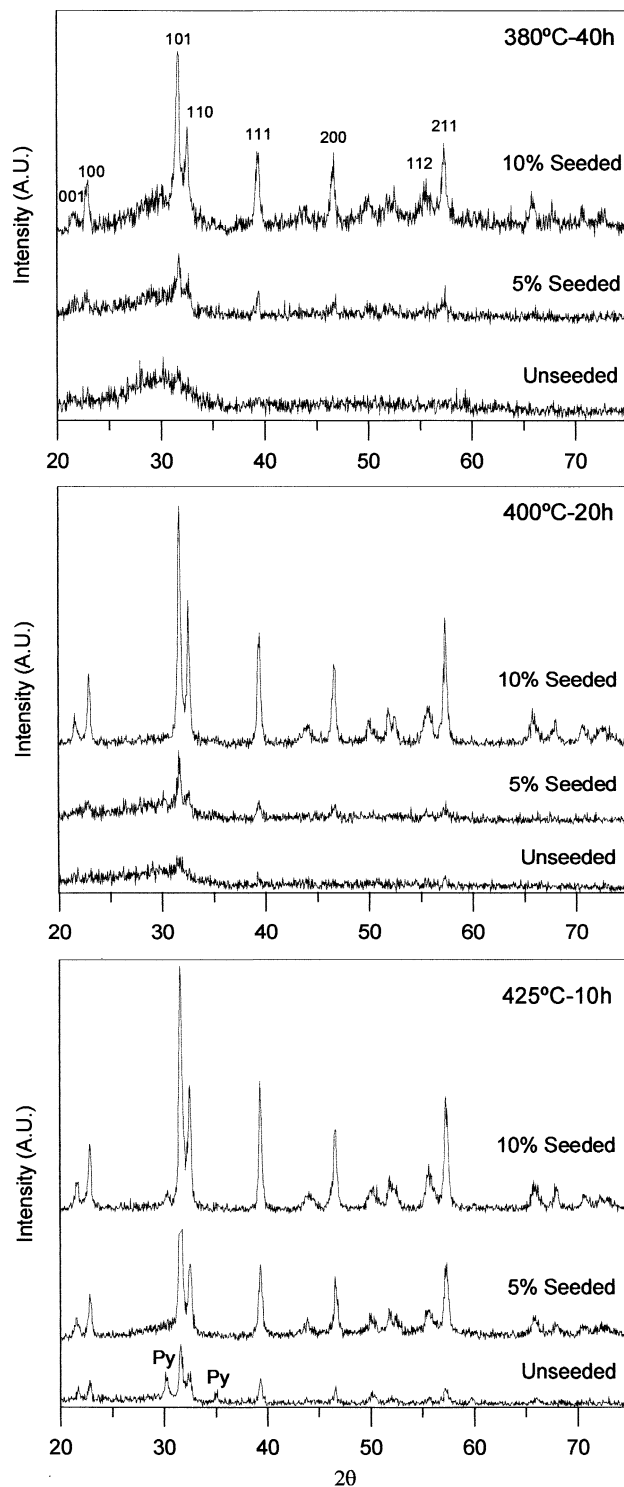Fig. 2. DTA and TGA curves of unseeded and 5, 10 wt% seeded gels.

Fig. 3. XRD analysis of unseeded and 5, 10 wt% seeded gels calcined at 380°, 400° and 425°C. Py (Pyrochlore phase).
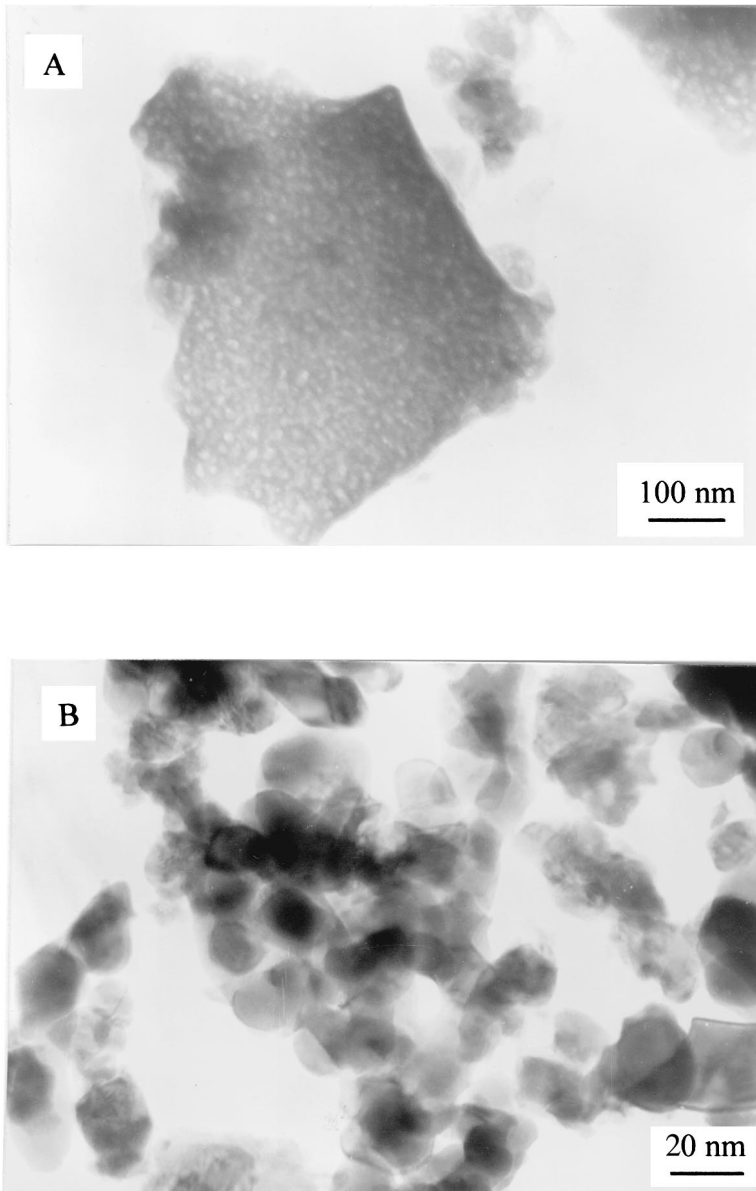
Fig. 4. TEM micrographs of unseeded (A) and 10 wt% seeded gel (B) calcined at 400°C for 20 h.

for the 5 wt% seeded gel, and for 10 wt% seeded gel, with 90% of crystallisation, the pyrochlore phase was also detected but in much lower proportion than in unseeded $PbTiO_3$ gel.

The different degree of crystallisation was also observed by TEM, Figure 4. For the morphology analysis of calcined gels, dried monoliths of unseeded and 10 wt% seeded gels were grinded and then calcined at 400°C for 20 h. It can be noted that the morphology of the

10 wt% seeded gel powder consisted of crystallites with sizes of about 20 nm. By contrary, the unseeded air-calcined sample showed the poorly developed tetragonal $PbTiO_3$ particles.

4. Discussion

The above results show that an increasing of the nucleation sites, by seeding, lowers the temperature onset of the crystallisation of $PbTiO_3$. On the other hand, such an increasing of the nucleation sites results in an enhancing of the nucleation rate and giving rise therefore, to enhanced crystallisation kinetics for each temperature. These results are consistent with the fact that in the case of a heterogeneous nucleation process, as it can be considered the present case, the presence of the nanometric size $PbTiO_3$ seed particles, being isostructural with the final $PbTiO_3$ product and having a close lattice matching between them, will favour a decreasing of the activation energy for nucleation and reducing, thus, the overall energy requirements for epitaxial growth from the provided nuclei of the new synthesized $PbTiO_3$ phase [11]. In addition, the increased rate of crystallisation for seeded gels could affect, lowering, the presence of pyrochlore phase, as the results of the present work have shown. Seifert et al. [12], explained that the free energy change for crystallisation of the perovskite phase is large and kinetically limited at low temperature and thus metastable phases, as pyrochlore, crystallise. Then, considering that the perovskite phase is the thermodynamically stable one, the appearance of pyrochlore phase could be explained on the basis of a formation rate higher than that of perovskite. Given that for seeded gel the crystallisation of the $PbTiO_3$ phase is significantly improved respect to that of unseeded gel, it could be assumed that the addition of nanocrystalline $PbTiO_3$ particles favours by decreasing the activation energy and/or by improving the crystallisation kinetic of $PbTiO_3$, the formation of $PbTiO_3$ phase in detriment of other secondary phases as pyrochlore. It must be considered that the temperature should be enough for nucleation on the seeded particle but also low enough to prevent nucleation of the unseeded area of the gel where the formation of $PbTiO_3$ phase was not so favoured and, therefore secondary phases could also appears. For this reason, 10 wt% seeded samples calcined at 400°C did not exhibit traces of pyrochlore, but increasing the temperature at 425°C promote the presence of this phase. Liu et al. [13] showed that a careful control over nucleation of the desirable perovskite phase in $PbTiO_3$ sol-gel derived films produced the perovskite phase by direct formation from the amorphous precursor. Indeed, as the results of this work indicate, this control over nucleation can be performanced by seeding, and thus, thermodynamically metastable phases may be avoided and the perovskite phase is formed via nucleation control.

5. Conclusions

The addition of solid $PbTiO_3$ nanometer-size seed particles (5 and 10 wt%) into the precursor solution plays a crucial role during crystallisation. Comparing with the unseeded gels, the fraction of crystallised $PbTiO_3$ increases at the same calcining temperature. The mechanism for which such a process takes place is assumed to be a catalysed nucleation by

the seeding with nanometric PbTiO$_3$ particles. The seeds being isostructural with the expected equilibrium phase and, therefore, having a close lattice matching, helps to control the thermodynamics of the formation reaction of the PbTiO$_3$. In addition, seeding reduces or even inhibits the presence of pyrochlore secondary phases and, deficient lead phases such as PbTi$_3$O$_7$ were not detected, even without the addition of PbO in excess. Both effects are attributed, in principle, to the improved crystallisation rate of the perovskite phase in detriment of other secondary phases. A study of the crystallisation kinetics and the calculation of the activation energy would be recommended to verify these assumptions. This work is currently in progress.

Acknowledgments

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