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Influence of seeding on the crystallisation kinetics of $PbTiO_3$ from gel-derived precursors

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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 $PbTiO_3$ nanoparticles (5 and 10 wt.%) into the precursor solution affects the crystallisation process. Thus, unseeded gel calcined at 380°C remained almost amorphous whereas 10 wt.% seeded gel was $>70\%$ crystallised. At 400°C, the 10 wt.% seeded sample was almost fully crystallised and the pyrochlore phase was not observed. The isothermal crystallisation kinetics for an unseeded and 5, 10 wt.% seeded $PbTiO_3$ have been compared. The seeded one exhibited enhanced crystallisation kinetics and the activation energy for the $PbTiO_3$ crystallisation was reasonably lowered (from 281 kJ/mol for unseeded to 121 kJ/mol for 10 wt.% seeded gel). © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sol–gel processes; B. X-ray methods; Lead titanate; Crystallisation

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 aging rate of the dielectric constant [1]. Therefore, $PbTiO_3$ is useful as pyroelectric and piezoelectric material for high temperature or high-frequency applications such as nonvolatile memories, infrared sensors, microactuators, capacitors, and electrooptic 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]. As an alternative, a sol–gel process using inorganic precursors, $TiCl_4$ and $Pb(NO_3)_2$, has also been reported [4].

Properties of these ceramics are strongly related to the stoichiometry. The presence of pyrochlore, a metastable intermediate phase, and/or lead-deficient secondary phases, $PbTi_3O_7$, can damage significantly the electrical properties. Calzada et al. [5] reported that the formation of lead deficient phases delay and even hinder the formation of perovskite. Therefore, the incorporation of an excess of PbO (up to 20 mol%) to compensate the lead oxide losses produced during heating, is necessary for obtaining the single perovskite phase without other crystalline structures. However, an excess of lead oxide can make the microstructure control difficult. Kim et al. [6] reported a very important result, crack-free, undoped $PbTiO_3$ ceramics were prepared via sol–gel without excess of lead. Therefore, the preparation of $PbTiO_3$ ceramics in stoichiometric proportion was recommended.

Currently, the controversy is whether the perovskite phase can crystallise directly from the amorphous gel or, the pyrochlore phase, referred as the low-temperature stable phase of lead titanate, is an intermediate phase previous to the formation of $PbTiO_3$. Carper et al. [7] reported a sol–gel process for the preparation of grain oriented thin films of $PbTiO_3$, using an atomic ratio of $Pb/Ti = 1.1$. The $PbTi_3O_7$ phase in these films was not observed because the excess of lead. However, the possibility was mentioned that certain portions of the film may have undergone local ordering in the form of an oxygen-deficient pyrochlore structure and this phase disappeared with heat treatment at higher temperatures (>600°C). Seifert et al. [8] explained that the free energy

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change for crystallisation of the perovskite phase is large and kinetically limited at low temperature and thus metastable phases, as pyrochlore, crystallise. A careful control over homogeneity of the sol–gel mixture is required to form directly the perovskite phase from the amorphous precursor.

Thus, the purpose of this work is the applying of the "seeding fundamental concepts" [9,10] to the preparation of $PbTiO_3$ by sol–gel, from stoichiometric amounts of titanium and lead. Seeding of lead-derived titanates have been studied previously, Zaghete et al. [11] 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. In a previous work, [12] the effect of seeding on the crystallisation temperature and rate of crystallisation of Y-TZP system have also been studied. Based on those results, lower crystallisation temperature and/or increase of the crystallisation kinetic of the $PbTiO_3$ perovskite phase are expected, and they could be the keys to reduce or even inhibit the appearance of secondary phases.

2. Experimental procedure

The preparation process is based on that proposed by Kumar [13]. 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 h to ensure the formation of the intermediate precursor phase based on Pb–O–Ti bonding. 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, free of secondary phases, were suspended in pure isopropanol and added to the transparent sol in a concentration of 5 and 10% of the total weight. These ones were previously, prepared by this same method and heated at 550°C. The crystallite size of the seeds was ≈50 nm, as determined from the analysis of X-ray line broadening using the Sherrer formula [14]. 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 hydrolyzed sol was sufficient to avoid the deposition of seeds. Then, the gel was deposited on a cristallisator and dried at 60°C for 72 h. A differential thermal analyzer (DTA/TG, Netzsch STA-409) was used to study the maximum temperatures of the crystallisation process. Dried gel monoliths were heated in a small platinum crucible for soaking times which varied from 1 h up to 160 h in an isothermal mode in the temperature range of 380 to 425°C. After heating the amount of crystallised tetragonal phase was measured by X-ray diffraction (Siemens D5000 with CuK_α) on the 111 peak area using a previously calibrated curve. Powder morphology was observed by Transmission Electron Microscopy (Hitachi H 7000).

3. Results and dscussion

3.1. Crystallisation characteristics

DTA and TGA curves of unseeded and 5, 10 wt%. seeded samples heated from 25°C to 600°C in air, are shown in Fig. 1. First, a weight loss of about 27% appears at temperatures around 240°C, 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

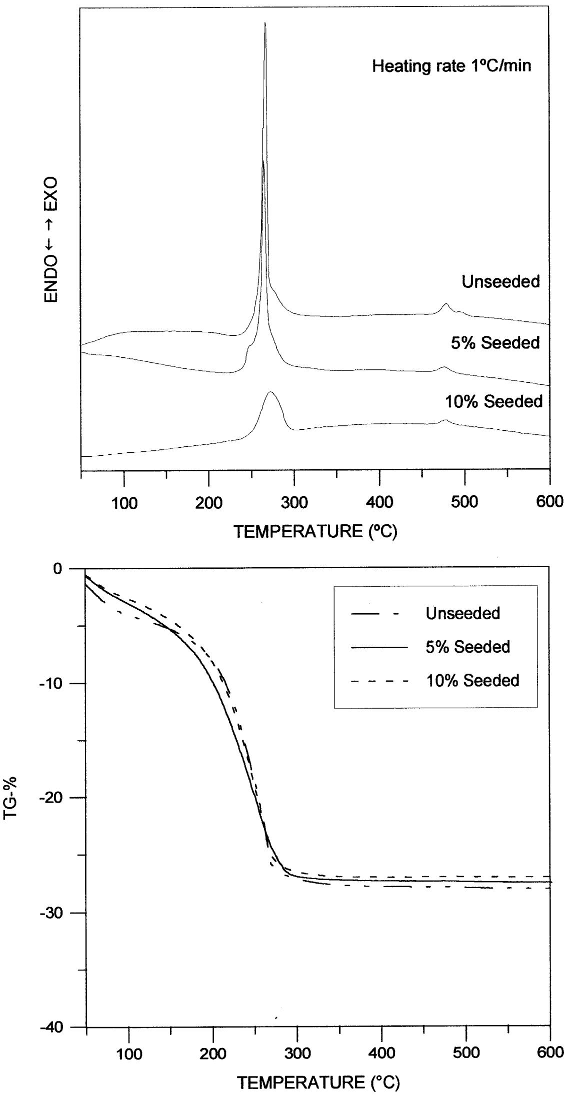

Fig. 1. DTA and TGA curves of unseeded and 5, 10 wt.% seeded gels.

phase transformation to the crystalline perovskite phase. The presence of two peaks in the case of unseeded samples could be explained, if it would exist two different size groups of the precursor powder since the smaller one crystallise at lower temperature, as Han et al. [15] explained. However, in this case it is not possible assuming that the precursor is a complex alkoxide containing Pb–O–Ti bonding [16]. Other possibility is that organic residuals still remain in the unseeded material, however the TGA of these samples, did not show weight losses in that range of temperature.

XRD analysis of unseeded and seeded samples calcined at temperatures of 380, 400 and 425°C (Fig. 2), 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 h whereas 10 wt.% seeded gel was $>70\%$ crystallised (Fig. 3). At 400°C for 20 h the unseeded sample showed about 20% of crystallisation and the 5 and 10 wt.% seeded samples heated at the same conditions were 50 and 85% crystallised, respectively. The different degree of crystallisation was also

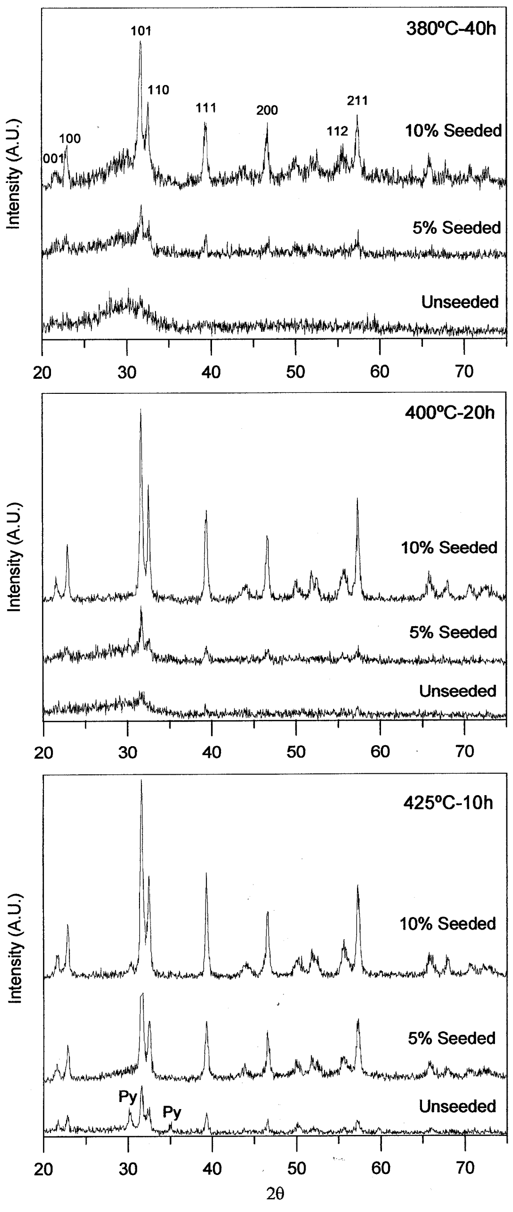

Fig. 2. XRD analysis of unseeded and 5, 10 wt.% seeded gels calcined at 380, 400 and 425°C. Py (pyrochlore phase).

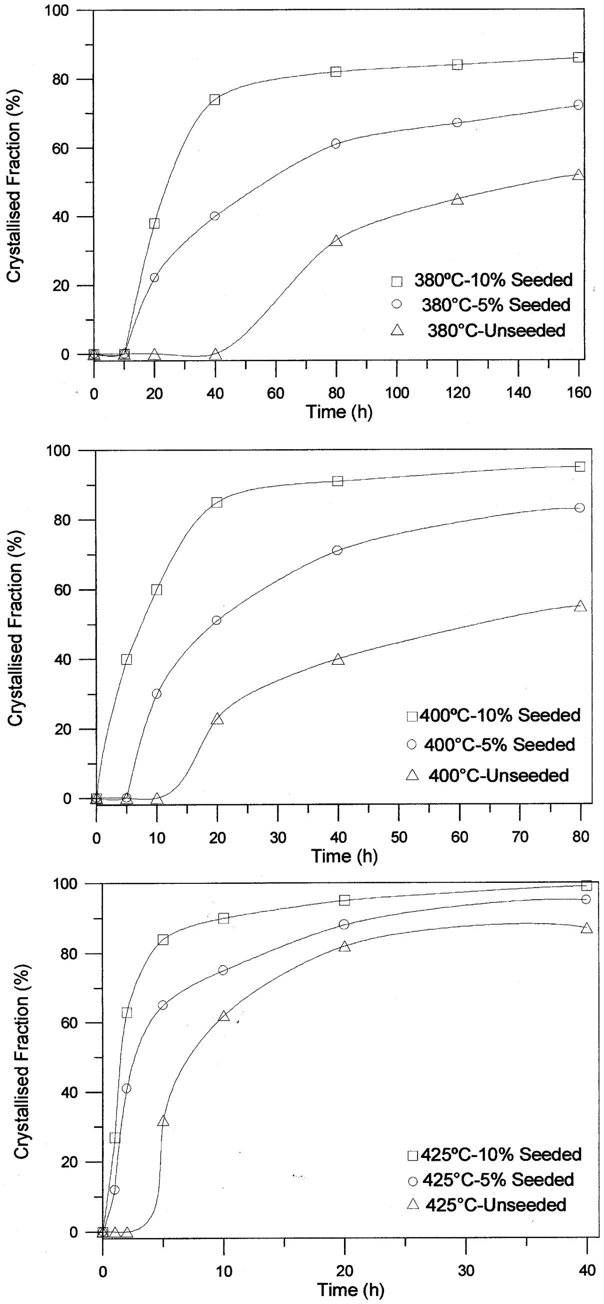

Fig. 3. Isothermal kinetics for the $PbTiO_3$ crystallisation at 380, 400 and 425°C as a function of the $PbTiO_3$ seed concentration.

observed by TEM. Fig. 4 shows the micrographs of the gel powders calcined at 400°C for 20 h. It can be noted that the morphology of the seeded gel powders, consisted of crystallites with sizes of about 20 nm. By contrary, the unseeded one showed the poorly developed tetragonal $PbTiO_3$ particles. It can be explained assuming that $PbTiO_3$ seeds, homogeneously distributed, promoted a heterogeneous nucleation of the $PbTiO_3$ perovskite phase. The rapid crystallisation of the newly forming phase was favoured, presumably, because of epitaxial growth on the surface of the isostructural crystalline $PbTiO_3$ seed nanoparticles. The epitaxial crystallisation phenomenon has also been evidenced in many other seeded-gels to ceramic transformation with nanosized particles [17–19]. Considering that, as shown in the DTA results, the lowering of the crystallisation temperature by seeding is not very significant, $\approx$25°C, it can be assumed that the $PbTiO_3$ seeds mainly accelerate the rate of crystallisation, thus increasing the amount of crystalline $PbTiO_3$ formed by providing a great number of nuclei with the same structure of the final $PbTiO_3$ phase. In any case, it is important to note that the crystallisation of $PbTiO_3$ starts at temperatures as low as 380°C. Kwon et al. [20] reported that the oxidation reaction of the organic components is highly exothermic so, the generated thermal energy may induce the nucleation for the perovskite phase even though external temperature is not high enough for its formation. Other consideration for explaining the low temperature formation of perovskite phase is given by Fukui [1]. An adequate reaction time is required for obtaining appropriate degree of polymerisation of the condensation product, longer reaction time for the complex alkoxide synthesis tends to increase the perovskite content at lower temperatures. This fact has also been taken into account in our experimental procedure, maintaining the precursor solutions under constant stirring during 24 h to ensure the formation of the intermediate precursor phase based on Pb–O–Ti bonding. Finally, Schwartz et al. [21] concluded that the reduced temperatures for crystallisation obtained by chemical methods compared with conventional routes are associated with lower activation energies. For this reason, a calculation of the activation energy is undertaken in the present work in an attempt to explain such a low crystallisation temperature, especially for the cases of seeded gels.

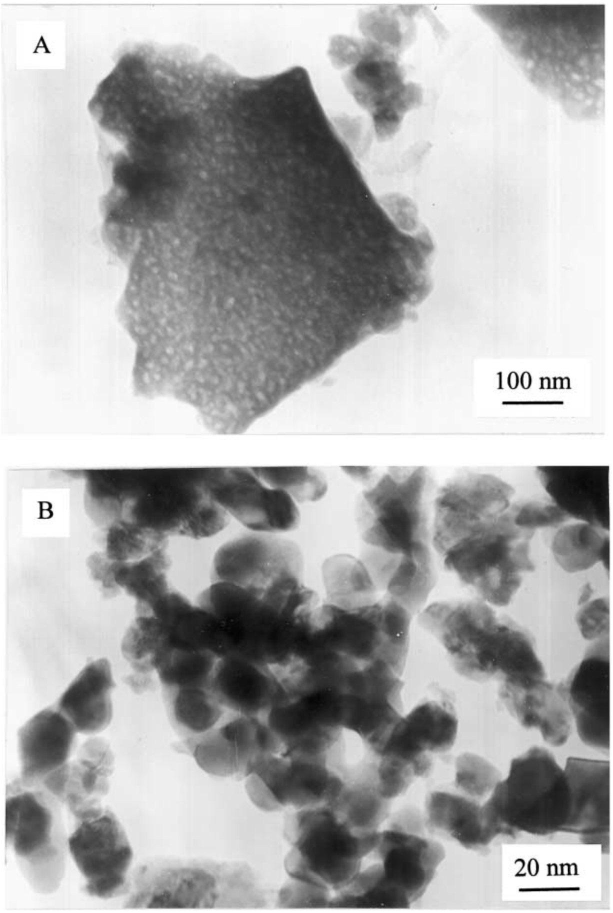

Fig. 4. TEM micrographs of (A) unseeded and (B) 10 wt.% seeded gel calcined at 400°C–20 h.

The other aspect to be considered is the presence of the pyrochlore phase. First, this phase was not observed by XRD (Fig. 2), in 10 wt.% seeded gels calcined at 400°C for 20 h. Whereas the unseeded calcined gels clearly exhibit the presence of pyrochlore phase at 425°C for 10 h, such a phase was not detected for the 5 wt.% seeded gel calcined at this temperature, and for 10 wt.% seeded gel with a 90% of crystallisation the pyrochlore phase is now observed but in much lower proportion than in unseeded which exhibit a 62% of crystallisation. Carim et al. [22] proposed two distinct mechanisms for the perovskite formation. First, the perovskite phase is formed from the pyrochlore phase (more stable at lower temperatures than perovskite), and the other possibility involves a simultaneous crystallisation of both phases from amorphous. The crystallisation of unseeded gels seems to occur, assuming the high fraction of pyrocholore, by the first mechanism. By contrary, seeded gels would crystallise following the second mechanism. In the 5 wt.% seeded gel the pyrocholore is not detected, probably because the small grain size, but in 10 wt.% seeded gel, where the degree of crystallisation is larger, the pyrocholore is already detected. From these results, it could be assumed that the previous or simultaneous crystallisation of the pyrochlore phase respect to the perovskite or even the direct crystallisation of this last one from amorphous precursor might be a kinetic issue. To clarify these points a study of the crystallisation kinetics and the calculation of the activation energy are now undertaken.

3.2. Crystallisation kinetics

If the crystallisation of tetragonal $PbTiO_3$ phase could be considered as a nucleation and growth process, then by plotting the fraction of crystallised $PbTiO_3$ phase as a function of time, curves of the sigmoidal shape should be obtained in close agreement with the Avrami model [23] which assumes that growth is controlled by diffusion. Fig. 3 shows such plots for unseeded, 5 and 10 wt.% seeded $PbTiO_3$ precursors at 380, 400 and 425°C. From these curves it seems evident that the kinetics of the $PbTiO_3$ crystallisation were reasonably enhanced by seeding $PbTiO_3$ amorphous precursors with nanocrystalline $PbTiO_3$ particles. As established by the Avrami-type nucleation and growth kinetics [23], an induction time in which no crystallisation was detected seems to exist. In our case, such an induction time was obtained by extrapolation of the linear part of the sigmoidal crystallisation curves to 0.5% of $PbTiO_3$ phase. Thus, as it can be observed, the induction time for the seeded $PbTiO_3$ crystallisation was reduced about one order of magnitude by comparison to the unseeded $PbTiO_3$ at the same temperature.

According to the above assumption, the Avrami transformation kinetic expression [23] was used to evaluate the XRD data. The relationship between volume fraction and time is given by

$$x = 1 - \exp(-kt^n)$$

where n is a constant dependent on the nucleation and growth mechanisms, and k is the rate constant. For isothermal conditions, the experimental data were better fitted according to the following linear transformation of the above equation:

$$\mathrm{Ln}[-\mathrm{Ln}(1-x)] = \mathrm{Ln}k + n\mathrm{Ln}t$$

where x is the weight fraction of crystallised $PbTiO_3$ phase. Plots of $\mathrm{Ln}[-\mathrm{Ln}(1-x)]$ as a function of Ln t (Fig. 5) yield the values of n and k. The rate constants, shown in Table 1, were determined from the intercept with ordinate axe at each isothermal temperature. As it is shown, comparable rate constants were measured at temperatures 45°C lower in seeded $PbTiO_3$ gels relative to unseeded samples. The temperature dependence of k apparently follows an Arrhenius relationship, according to:

$$k = A\exp(-E_a/\mathrm{RT})$$

where A is the frequency factor, E_a the apparent activation energy of crystallisation, and R the gas constant. Plots of Ln k vs 1000/T, as shown in Fig. 6, yielded straight lines with very good correlation coefficients, $\geqslant 0.999$ for seeded samples and $\geqslant 0.99$ for unseeded one. The activation energies calculated were 281 ± 14 kJ/mol for the unseeded, 180 ± 5 kJ/mol and 121 ± 4 kJ/mol for the 5 and 10 wt.% seeded $PbTiO_3$ amorphous precursors gel, respectively. Clearly, the activation energy of crystallisation obtained in the case of seeded $PbTiO_3$

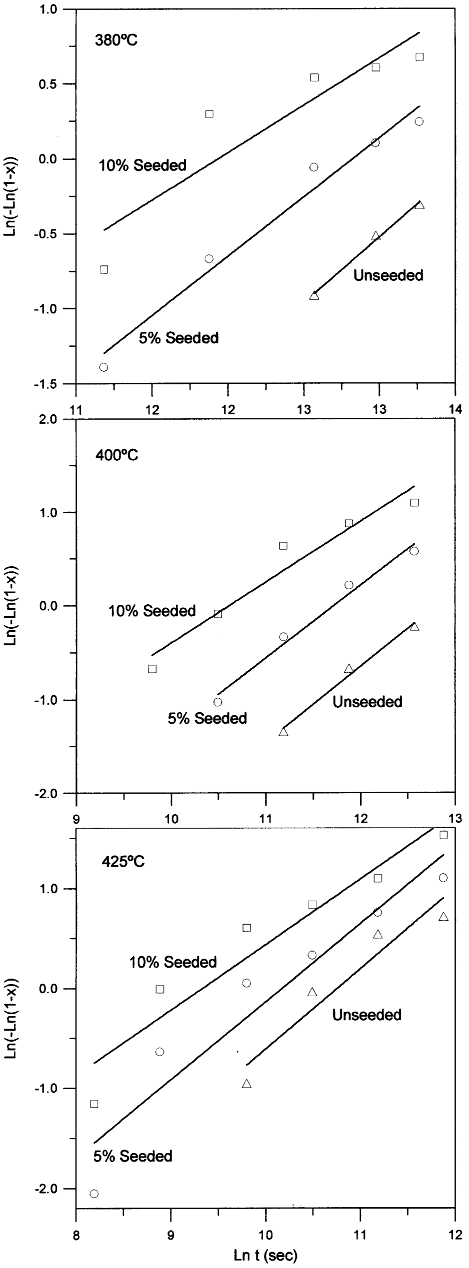

Fig. 5. Avrami plots for the $PbTiO_3$ crystallisation at 380, 400 and 425°C as a function of the $PbTiO_3$ seed concentration.

Table 1
Kinetic constant, k, and activation energy, E_a, for the crystallisation of unseeded, 5 and 10 wt.% seeded $PbTiO_3$ amorphous precursors

Temperature (K)	k (s^{-1})		
	$PbTiO_3$ unseeded	$PbTiO_3$, seeded 5 wt.%	$PbTiO_3$, seeded 10 wt.%
653	6.25×10^{-6}	3.97×10^{-5}	5.35×10^{-4}
673	3.31×10^{-5}	1.15×10^{-4}	1.01×10^{-3}
698	1.77×10^{-4}	3.59×10^{-4}	2.24×10^{-3}
E_a (kJ/mol)	281 ± 14	180 ± 5	121 ± 4

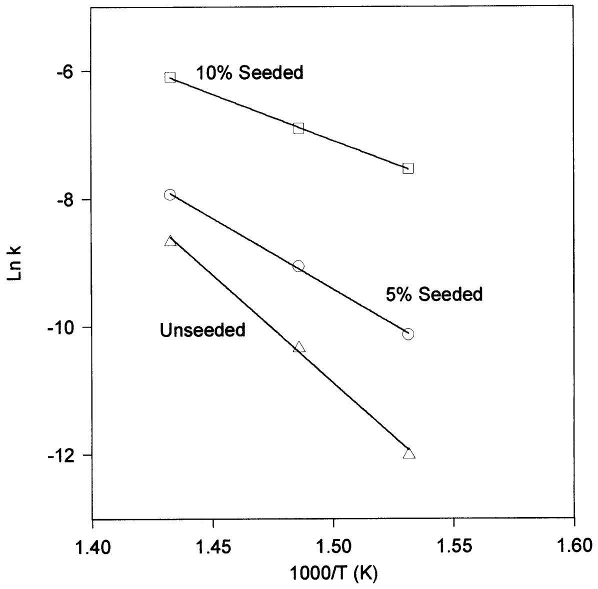

Fig. 6. Arrhenius plots of crystallisation rate constant for calcined unseeded and 5, 10 wt.% seeded gels.

amorphous precursor gel is much lower than the unseeded one. This last value is in close agreement with those reported by Schwartz et al. [21] obtained for crystallisation of sol–gel derived $PbTiO_3$ by differential scanning calorimetry.

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 sized $PbTiO_3$ seed particles requires a much smaller activation energy to reach the critical nuclei size [24]. Then we can conclude that the seeding of $PbTiO_3$ precursors with nanocrystalline $PbTiO_3$ particles has a significant effect on the crystallisation process, (a) by lowering the onset of the crystallisation temperature and mainly (b) by enhancing the crystallisation kinetics at each temperature. From the above results, it could be also stated that the characteristics of the seed $PbTiO_3$ nanometric particles, being isostructural with the final $PbTiO_3$ product and having a close lattice matching between them, will favor 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 [24]. Such a growth process could take place by a surface diffusion mechanism that needs low activation energy to be carried out. The obtained values of activation energy support the statement that the presence of nanometric $PbTiO_3$ seed particles lowers the activation energy to reach the critical nuclei size and, thus, the activation energy for the crystallisation process of the $PbTiO_3$ from amorphous gel.

In addition, the lowered activation energy and the increased rate of crystallisation in seeded gels could affect, lowering, the presence of pyrochlore phase, as the results of the present work have shown. Moon et al. [2] report no evidence of crystalline intermediate precursor materials such as pyrochlore or fluorite phases in oriented lead titanate, obtained by sol–gel method on particle-seeded substrates. They explained that the temperature should be sufficient for nucleation on the seeded particle but also low enough to prevent nucleation in the unseeded area of the substrate where the formation of $PbTiO_3$ phase was not so favored. Therefore secondary phases could also appear. This is what probably occurs in our case. In 10 wt.% seeded gels calcined at 400°C, the pyrochlore phase is not detected, but increasing the temperature to 425°C, promote the presence of this phase. Liu et al. [25] also mentioned that a careful control of nucleation of the desired perovskite phase in $PbTiO_3$ sol–gel derived films produced the perovskite phase by direct formation from the amorphous precursor. Indeed, this control of nucleation can be performed by seeding, and thus, thermodynamically metastable phases occurrence may be reduced or even avoided. 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 [8]. Therefore, the addition of nanocrystalline $PbTiO_3$ particles, being isostructural with the final $PbTiO_3$, favors the crystallisation kinetic of $PbTiO_3$.

4. Conclusions

The additions of solid PbTiO3 nanometer-size seed particles (5 and 10 wt.%) into the precursor solution play a crucial role during crystallisation. Comparing with the unseeded gels, the fraction of crystallised $PbTiO_3$ increases for the same calcination 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, help to control the thermodynamics of the formation reaction of the $PbTiO_3$. The isothermal crystallisation process is best fitted by an Avramy-type kinetic relationship for a random nucleation which enhancing the crystallisation rate of $PbTiO_3$, with activation energies of 281 ± 14 kJ/mol for the unseeded, 180 ± 5 kJ/mol and 121 ± 4 kJ/mol for the 5 and 10 wt.% seeded $PbTiO_3$ amorphous gel precursors, respectively.

In addition, seeding reduces or even inhibits the presence of secondary pyrochlore phase and, deficient lead phases such as $PbTi_3O_7$ were not detected, even without the addition an excess of PbO. Both effects are attributed, in principle, to lower activation energy required to nucleate the $PbTiO_3$ phase from the seeds and the improved crystallisation rate of the perovskite phase in detriment of other secondary phases.

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