

# Phase transformations in sol–gel prepared $\text{PbTiO}_3$

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The sol–gel preparation of  $\text{PbTiO}_3$  by two different methods is reported. Both methods began with titanium isopropoxide and lead acetate as organic precursors, but without or with hydrochloric acid as catalyst, respectively. Preparation procedures and working atmosphere also differed. The crystallization by thermal treatments and laser annealing was followed by XRD and Raman spectroscopy. When no hydrochloric acid was used, an intermediate pyrochlore phase,  $\text{Pb}_2\text{Ti}_2\text{O}_6$ , was observed during the thermal treatment, and the final perovskite was obtained together with  $\text{PbTi}_3\text{O}_7$  as the minor phase. Using the catalyst, the pure perovskite,  $\text{PbTiO}_3$ , was obtained through an unidentified phase appearing at the beginning of the crystallization process. Frequency changes in the Raman spectra during the crystallization are attributed to pressure effects on the microcrystals.

## 1. Introduction

Lead titanate,  $\text{PbTiO}_3$  (PT), is a perovskite-type ferroelectric material with interesting dielectric, pyroelectric and piezoelectric properties [1]. Its large pyroelectric coefficient and electro-mechanical coupling factor have made PT a good candidate material for applications such as detectors, capacitors, piezoelectric actuators, and integrated non-volatile memories. At room temperature, PT has a tetragonal perovskite structure [2] and, when combined with other oxides, forms a series of materials as  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT),  $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$  (PLZT) whose very wide range of applications is well established. For films and powders of PT-based materials, the development of pure perovskite phase is required to obtain the ferroelectric properties.

The sol–gel process is a chemical technique which is well suited to obtain powders, ceramics and thin films of many materials, and offers several advantages with respect to traditional techniques such as low processing temperatures, high purity and homogeneity of the products, a wide range of obtainable materials. In addition, the sol–gel method allows the realization of amorphous materials which cannot be obtained with other methods. The sol–gel process involves the preparation of a polymerizable solution which is diluted and partially hydrolysed. A polymeric gel is formed and the resulting dried amorphous bulk is further heat treated to remove the organic residuals and to obtain the crystalline phases. Sol–gel derived PT powders have been reported to crystallize directly into the perovskite structure [3], while thin films often form first into the cubic paraelectric pyrochlore phase [4, 5] and subsequently transform into perovskite at higher (500–700 °C) temperatures. X-ray diffraction (XRD)

and Raman spectroscopy are useful techniques to characterize the phases obtained during the crystallization by heat treatments of sol–gel derived powders [6]. In this work, two different methods to prepare PT are reported and the obtained phases are investigated for a better understanding of the crystallization process and to optimize the degree of purity of the final perovskite.

## 2. Experimental procedure

Two different preparation methods, A and B, were used.

(A)  $\text{PbTiO}_3$  gel was obtained from the precursors, titanium isopropoxide,  $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$ , and lead acetate,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ . The whole process was performed under a nitrogen atmosphere and with the use of a “dry box”. The final solution was prepared using methoxyethanol as the solvent to ensure a good solubility of the lead titanate.

(B) The starting materials and the solvent are the same as before, but hydrochloric acid was added to the solution as a catalyst and the whole process was completed in air. This method is simpler and allows a better control of the stoichiometry.

The sols obtained by both methods gelled in air at room temperature in few days. The as-obtained gels were dried at 125 °C for 1 h, then powdered and heat treated from room temperature to 800 °C at the heating rate of 100 °C h<sup>-1</sup> to study the crystallization process.

A third solution was prepared following procedure A, but by mixing lead and titanium precursors in molar ratio 1:2, respectively. The gel, obtained in air, was dried at 125 °C for 1 h and then heat treated at

700 °C for 1 h. XRD measurements performed on the treated powders revealed the presence of  $\text{PbTi}_3\text{O}_7$  as the only phase.

XRD patterns of the powders (treated at different temperatures) were obtained using a Philips PW 1050 Powder Diffractometer using  $\text{CuK}_\alpha$  radiation.

The unpolarized Raman spectra, taken on powders in capillary tubes or in pellets in a nearly back-scattering geometry, were obtained using the 514.5 and 488.0 nm light of a Coherent 2020 model cw  $\text{Ar}^+$  laser and collected by a SPEX 1403 double monochromator equipped with a Hamamatsu R 4362-2 photomultiplier and a photon counting system. The spectral resolution was set at about  $1 \text{ cm}^{-1}$ . The laser power during the measurements was kept low ( $<30 \text{ mW}$ ), to avoid uncontrolled thermal effects. The effective sample temperature was checked by Stokes and Anti-Stokes measurements [6].

In addition, the samples were heated at different laser powers (50–200 mW), focusing with a spherical lens for a few seconds and the Raman spectra were collected at low laser power after the heat treatment.

### 3. Results

#### 3.1. Method A

As reported in previous work [7], differential thermal analysis (DTA) performed on the gel indicates the solvent evaporation at  $\approx 130^\circ\text{C}$  and the combustion of the organics at about  $300^\circ\text{C}$ . The transition from the amorphous to a crystalline phase is evinced by a sharp exothermal peak at  $\approx 550^\circ\text{C}$ .

The XRD patterns of the heat-treated powder (Fig. 1) indicate that, up to  $500^\circ\text{C}$ ,  $\text{PbTiO}_3$  has an amorphous nature. At  $600^\circ\text{C}$  one observes the predominance of the pyrochlore phase with respect to the growing perovskite phase [8]. At  $700^\circ\text{C}$  the diffraction pattern corresponds to the perovskite phase, with no evidence of a pyrochlore phase, but the appearance of small peaks indicates that other minor phases are present. The nature of these phases cannot be determined by the XRD spectrum. Further heat treatments at  $800^\circ\text{C}$  produce no changes in the spectrum.

The Raman spectra of the powders are shown in Fig. 2. The amorphous nature of  $\text{PbTiO}_3$  up to  $500^\circ\text{C}$  is clearly in evidence [9]. The Raman spectrum of the dried gel shows a peak at about  $930 \text{ cm}^{-1}$ , ascribed to the residual organics [10], which disappears at the very beginning of the heat treatment.

The Raman spectrum of the pyrochlore phase is observed when the powder is heated at  $600^\circ\text{C}$ . This phase is usually observed only in thin films or by intentional introduction of dopants, such as silicon or zirconium [1, 8, 11]. Its Raman spectrum is characterized by a sharp peak at  $145 \text{ cm}^{-1}$  which has also been reported in the case of PZT films on a quartz substrate [12]. At  $700^\circ\text{C}$ , the Raman spectrum reproduces that of the well-known perovskite phase [2, 10] apart from several additional small peaks. As is already in evidence from XRD, at  $800^\circ\text{C}$  no changes in the spectrum are found.

The Raman spectrum observed is similar to that reported by other authors [10, 13, 14] for powdered

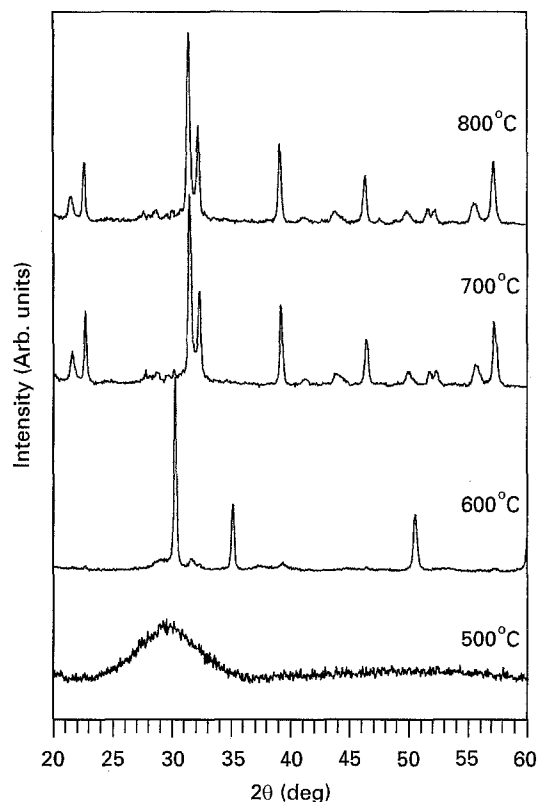


Figure 1 XRD patterns of  $\text{PbTiO}_3$  samples obtained by method A and treated at different temperatures.

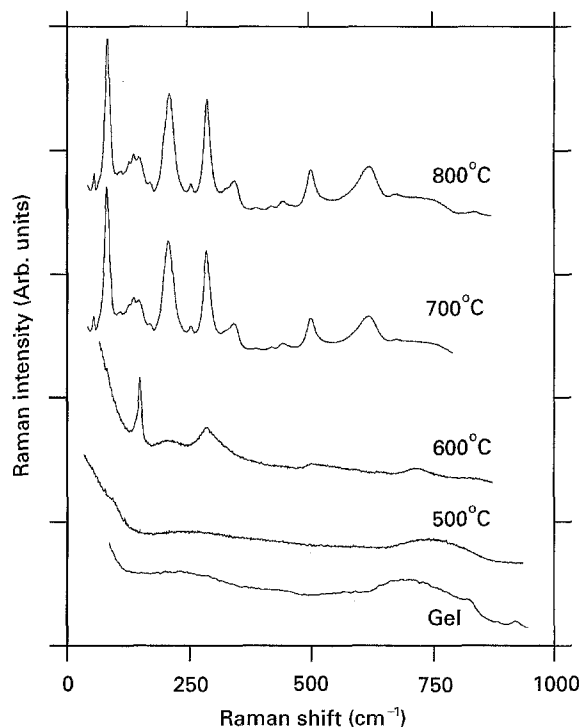


Figure 2 Raman spectra of  $\text{PbTiO}_3$  samples obtained by method A.

and thin-film samples and shows some peaks with slightly different frequencies with respect to the bulk single crystal.

Fig. 3 shows the spectrum of the  $\text{PbTi}_3\text{O}_7$  phase obtained by the sol-gel method: a close correspondence between its Raman features and the spurious peaks observed in the spectrum of the sample treated at temperatures  $\geq 700^\circ\text{C}$  may be found. The Raman

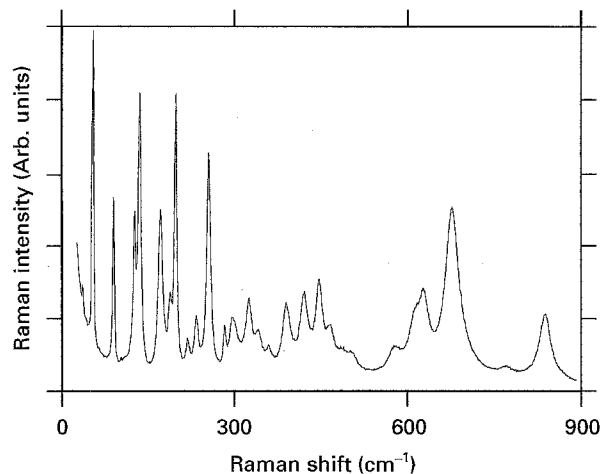


Figure 3 Raman spectrum of  $\text{PbTi}_3\text{O}_7$  obtained by the sol-gel method.

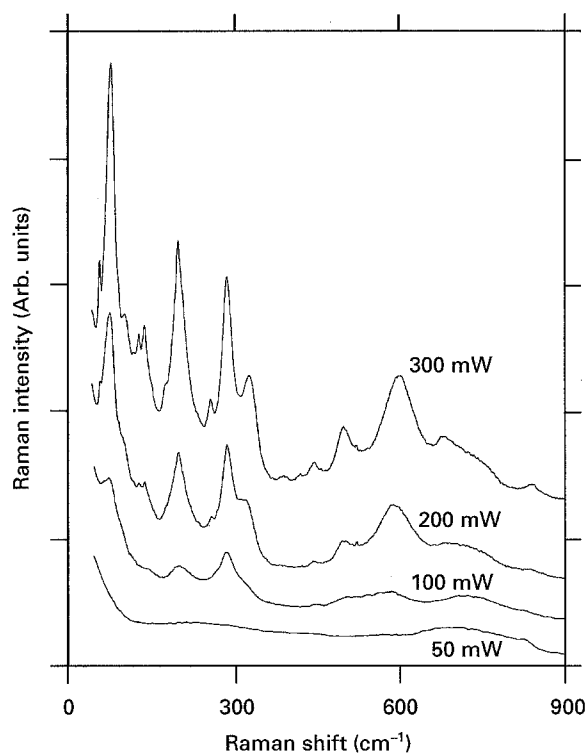


Figure 4 Raman spectra of  $\text{PbTiO}_3$  samples obtained by method A and annealed at different laser powers.

spectra on the laser-annealed samples (Fig. 4) shows no intermediate pyrochlore phase and the spectrum of the final phase is similar, with some differences in the Raman frequencies, to that measured in the samples heat treated at  $800^\circ\text{C}$ . The shape and the relative intensity of some peaks differ, probably due to a different proportion of the  $\text{PbTi}_3\text{O}_7$  phase with respect to the perovskite.

### 3.2. Method B

The XRD spectra (Fig. 5) show that up to  $370^\circ\text{C}$  the powder is amorphous, whereas at  $400^\circ\text{C}$  several small diffraction peaks indicate the presence of one or more crystalline phases, whose nature is undetermined [15]. At  $500^\circ\text{C}$ , the perovskite phase predominates and at

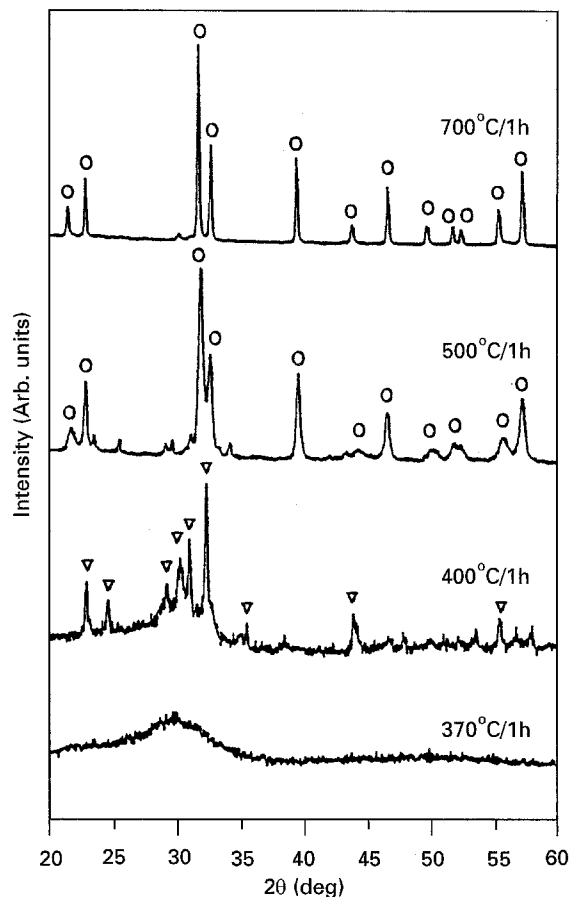


Figure 5 XRD patterns of  $\text{PbTiO}_3$  samples obtained by method B and treated at different temperatures. (○) Perovskite  $\text{PbTiO}_3$ , (▽) unidentified phase.

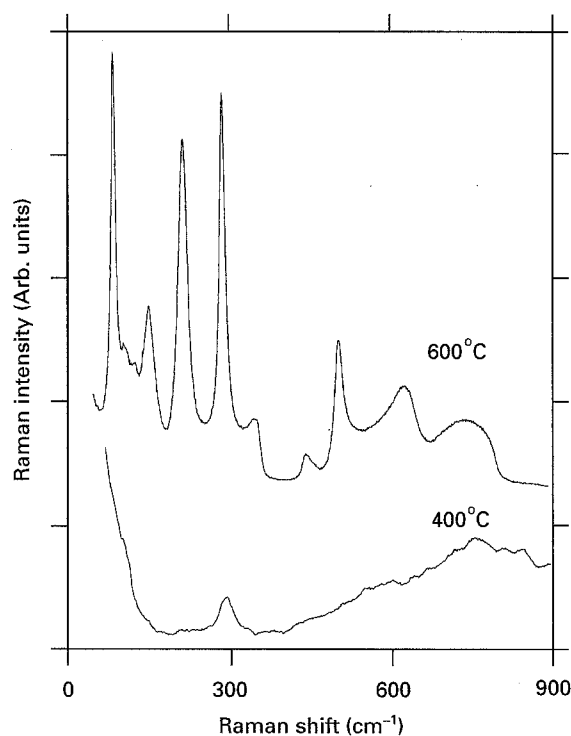


Figure 6 Raman spectra of  $\text{PbTiO}_3$  samples obtained by method B.

$700^\circ\text{C}$  one finally obtains the diffraction pattern of pure perovskite  $\text{PbTiO}_3$ .

The Raman spectra are shown in Fig. 6. The sample heated at  $400^\circ\text{C}$  shows a weak feature at about

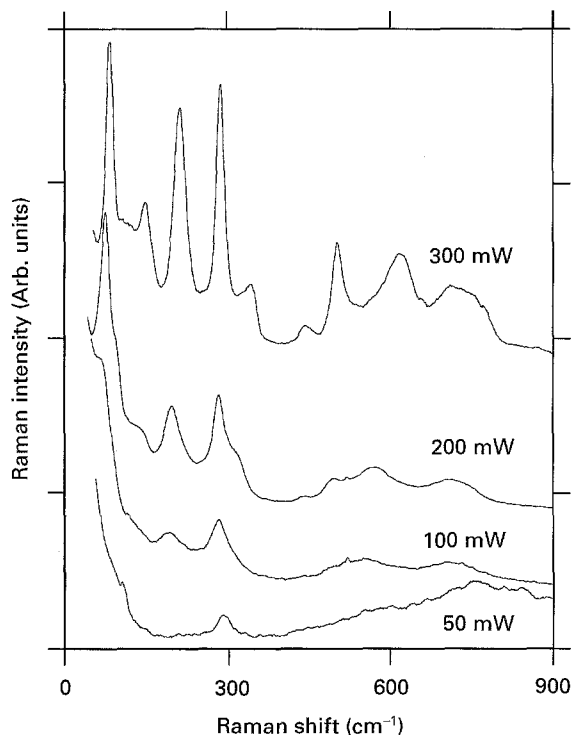


Figure 7 Raman spectra of  $\text{PbTiO}_3$  samples obtained by method B and annealed at different laser powers.

$290\text{ cm}^{-1}$  which evolves towards the strong  $288\text{ cm}^{-1}$  peak present in the perovskite phase. At higher temperatures the spectrum closely corresponds to that of the perovskite with no evidence of other crystalline phases.

The Raman spectra of the samples annealed at different laser powers (Fig. 7) evolve continuously from the amorphous phase to the pure perovskite phase, as observed in the heat-treated samples. As the perovskite phase grows, the main Raman peaks shift to higher frequencies.

#### 4. Discussion

The differences in the Raman frequencies observed in the final perovskite products with respect to the bulk crystal could be due to pressure effects on PT crystallites [16]. In sol-gel derived materials, the thermally induced crystallization starting from a gel generates some stress on the micrograins that form during the process [17]. The stress arises mainly from the densification of the solid due to the solvent evaporation as the temperature increases. The effect is more pronounced in the early stages of crystallization, when the dimensions of the micrograins, embedded in an amorphous matrix, are small, and the weight of the atoms in the stressed interfacial layers of the grains is greater. As crystallization proceeds the microcrystals increase their dimensions and a molecular rearrangement takes place, leading to progressive stress relaxation.

In addition, the  $\text{PbTiO}_3$  samples in the perovskite phase are ferroelectric, and this fact must be taken into account in discussing the vibrational properties [18]. When heat treated over  $500^\circ\text{C}$  to obtain the perovskite phase, the samples are composed by microcrystals

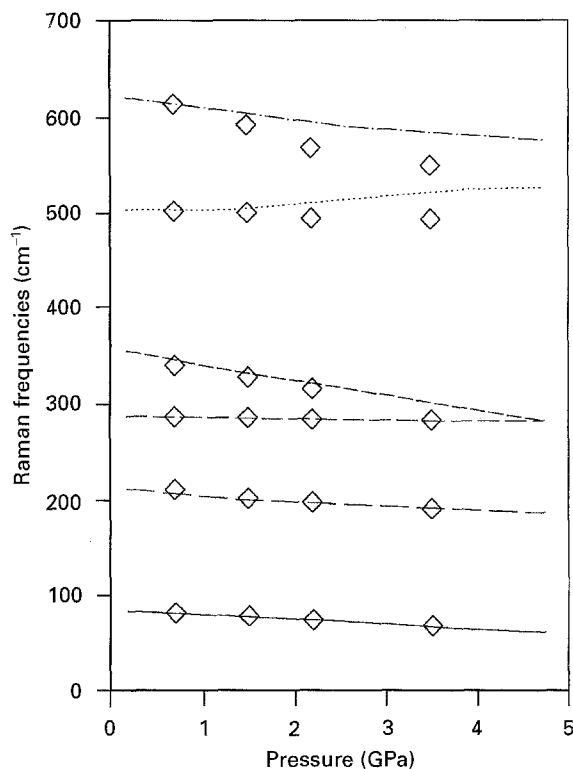


Figure 8 The change of some Raman frequencies of  $\text{PbTiO}_3$ , at various crystallization stages during laser annealing, compared with their pressure behaviour, as in [16].

tals in the cubic paraelectric state, because their crystallization temperature is greater than the Curie point ( $T_c = 490^\circ\text{C}$ ). As they are cooled to room temperature, the cubic to tetragonal deformation should take place. If the micrograins are too small to separate into ferroelectric domains, this deformation cannot take place because every grain is clamped by neighbouring grains with different orientations, leading to high stresses. Proceeding with heat treatments, the grains become larger and then able to separate into domains and the stress is released.

These sources of stress cause a hydrostatic pressure on the grains which can be interpreted as the principal source of the changes in the Raman frequencies of the samples during the crystallization process. Fig. 8 shows the frequencies of some Raman peaks measured on samples B at various stages of the crystallization during the laser-annealing process, together with the literature data [17] for the changes of the frequencies with respect to the hydrostatic pressure. The behaviour of the Raman frequencies as the crystallization proceeds is in good agreement with a progressive lowering of the pressure effect on the grains. This result agrees with a similar trend observed in  $\text{PbTiO}_3$  prepared using a melting technique [18, 19].

In microcrystalline systems the confinement effect may lead to the relaxation of the phonons wavevector selection rule,  $q = 0$ , and the contribution of the phonons with  $q \neq 0$  generates a broadening of the peaks and a related red-shift of the frequencies [20]. But this effect is predominant only in very small crystallites (with diameter less than 10 nm) and we ascribe the frequency shifts in our samples mainly to the pressure effects.

## 5. Conclusions

Lead titanate powders in the ferroelectric perovskite phase are obtained using the sol-gel process by two different methods. If no hydrochloric acid is used, the  $\text{PbTi}_3\text{O}_7$  phase appears together with perovskite as the final result of the heat treatments at 700 °C, and at about 600 °C a metastable paraelectric pyrochlore phase is observed. When hydrochloric acid is used as the catalyst, only pure perovskite phase is obtained as the final result. The Raman spectra of the perovskite phase show pressure effects due to the micro-crystalline structure of the powder.

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