# Preparation of monolithic crystalline lead titanate aerogels

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Lead titanate gels were prepared via sol–gel synthesis and dried either in supercritical carbon dioxide or isopropanol. Both types of aerogels were characterized by means of thermal analysis and transmission electron microscopy. Helium pycnometry and nitrogen adsorption measurements were performed on samples that had been annealed at temperatures up to 600 °C. Phase transformations and the crystallization of tetragonal $PbTiO_3$ were monitored by X-ray diffraction. While aerogels supercritically dried in carbon dioxide disintegrate upon heat treatment, samples dried in isopropanol can be transformed to the crystalline state as monoliths. With an envelope density of $0.75 \, g \, cm^{-3}$ these ceramics exhibit a porosity of 90%. © *1998 Chapman & Hall*

## 1. Introduction

Piezoelectric ceramics such as lead titanate ($PbTiO_3$, PT) and lead zirconate titanate ($PbZ_{0.53}Ti_{0.47}O_3$, PZT) are widely used as ultrasonic transducer materials [1]. Because the acoustic impedances of dense ceramics and gaseous media differ by several orders of magnitude, the efficiency of ultrasound emission in air is rather poor [2].

$SiO_2$ aerogels have been used as impedance matching layers [3]: thin slices of these highly porous inorganic materials on top of conventional ultrasonic transducers enhanced the performance of these devices up to 40 dB, because the acoustic impedance of aerogels ($2 \times 10^4 \, kg \, m^{-2} \, s^{-1}$) is closer to that of air ($4.1 \times 10^2 \, kg \, m^{-2} \, s^{-1}$) than the acoustic impedance of PZT ceramics ($3 \times 10^7 \, kg \, m^{-2} \, s^{-1}$). However, problems may arise from unsatisfactory bonding between the transducer and the aerogel layers. Thus preparation of porous piezoelectric materials, i.e. PT aerogels, offers a promising route for direct impedance matching [4, 5].

In our previous work [6–8] we have demonstrated that sol–gel processing and subsequent supercritical drying of the wet gels yield highly porous materials of lead titanate stochiometry. Even though cracking could be avoided during supercritical drying, crystallization of the yet amorphous aerogels is accompanied by shrinkage and cracking.

This paper describes a modified synthesis route for lead titanate wet gels which were dried supercritically either in carbon dioxide or isopropanol.

## 2. Experimental procedure

The lead titanate precursor solution was prepared based on a method described by Phillips *et al.* [9]: lead acetate trihydrate ($Pb(OAc)_2 \cdot 3H_2O$), dissolved in 1,3 propanediol at 80 °C, was added to an equimolar solution of titanium diisopropoxide *bis*acetylacetonate (Aldrich). The reaction mixture was refluxed at 150 °C for 4 h. Subsequent distillation at 20 mbar yielded a highly viscous brownish residue which was rediluted with 1,3 propanediol. This $PbTiO_3$ precursor solution contained 1 mol Pb and 1 mol Ti per litre as confirmed by chemical analysis.

Equal volumes of precursor stock solution and isopropanol containing 20 mol $H_2O$ per mol $PbTiO_3$ were mixed under continuous stirring. Gelation to yellowish monolithic gels occurred within 6–10 h. The gels were aged at 60 °C for 14 d in air-tight containers before the pore liquid was exchanged with pure isopropanol. A supercritical drying process either at 35 °C in carbon dioxide ($p > 7.5 \, MPa$) or at 236 °C in isopropanol ($p > 4.76 \, MPa$) yielded monolithic aerogels with the stoichiometry of lead titanate.

Envelope densities of aerogels were calculated from weight and volume; these results were confirmed by measurements on a GeoPyc envelope density analyser (Micromeritics Corporation, Norcross, GA, USA). Thermogravimetric analyses (thermogravimetric/differential thermal analysis, TG/DTA) (TAG-24, Setaram Scientific Instruments, Calcuire, France) were performed in dry air atmosphere or argon; heating rates of $10 \, K \, min^{-1}$ were applied. Differential

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scanning calorimetry (DSC) experiments were also performed under argon (DSC 7, Perkin-Elmer, Palo Alto, CA, USA). Samples of lead titanate aerogels for transmission electron microscopy (TEM) were ground and then dispersed on dry carbon films supported by copper grids. The analysis was performed on a transmission electron microscope (Philips CM-12).

Aerogel samples were treated at temperatures up to 600 °C in a preheated furnace for 1 h. After cooling in a desiccator, the skeletal density was determined by helium pycnometry (Ultrapycnometer 1000, Quantachrome Corporation, Boynton Beach, Fl, USA). X-ray diffraction patterns were recorded in Bragg-Brentano geometry (PW 1710, Philips Analytical Instruments, The Netherlands). Nickel-filtered $CuK_\alpha$ radiation was used under the operating conditions of 40 kV–35 mA. The specific surface area of aerogel samples was measured with an automated volumetric analyser (Micromeritics Corporation, Norcross, GA, USA); BET theory was applied [10].

# 3. Results and discussion
## 3.1. Drying of aerogels
Drying of lead titanate gels in supercritical carbon dioxide yields colourless opaque aerogels. During the drying process, shrinkage and cracking occur, and thin slices of the aerogels are transparent and appear bluish if illuminated from the side. This Rayleigh scattering phenomenon is typical for aerogels [11]. If gels are dried in supercritical isopropanol instead of carbon dioxide, shrinkage also takes place but only minor cracking is observed. The resulting aerogel is black and does not transmit light. Table I shows some characteristic data of the aerogels dried under different conditions.

The application of the new synthesis route yields $CO_2$-dried aerogels with lower envelope densities and higher porosities (Table I) than previously reported [7,8]. The network of the gel is strengthened and thus shrinkage during supercritical drying is reduced, but the resulting highly porous aerogel tends to crack more easily.

Aerogels obtained from supercritical drying of gels in isopropanol exhibit a higher envelope density, but

due to the increased skeletal density the resulting porosity is comparable to the $CO_2$-dried aerogels. This shrinkage and skeletal densification can be interpreted in terms of continued condensation reactions and thus stabilization of the network, because these aerogels remain monolithic after drying. The reduced specific surface area and C–H content in comparison to the $CO_2$-aerogels support this assumption.

## 3.2. Thermal analysis
Thermogravimetric analysis (TG) and differential thermal analysis were performed on the aerogels.

The aerogel dried from carbon dioxide loses 20% of its weight below 350 °C. This process is associated with two exothermal DTA signals (Fig. 1a). A third, broad, exothermal, signal between 450 and 550 °C is not related to any significant weight change.

The thermogravimetric analysis of the $CO_2$-dried lead titanate aerogel follows the pattern reported previously [6]. The endothermal removal of physisorbed solvent and water up to 150 °C is followed by the exothermal oxidative decomposition of chemically bonded organic surface groups. The burnout of organics is accompanied by two exothermal DTA signals. A further weak and broad exothermal peak can be observed at 510 °C without significant mass change. For lead titanate aerogels dried from carbon
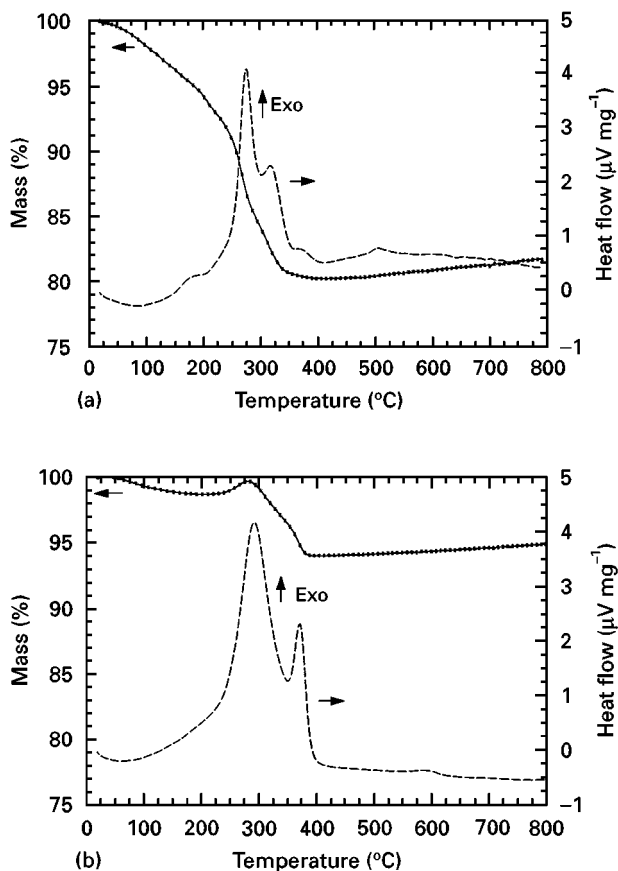
TABLE I Properties of lead titanate aerogels supercritically dried in carbon dioxide or isopropanol

|  | Carbon dioxide | Isopropanol |
|---|---|---|
| Envelope density, $\rho_{bulk}$ (g cm$^{-3}$)[a] | 0.40 | 0.60 |
| Skeletal density, $\rho_{skel}$ (g cm$^{-3}$)[b] | 3.7 | 4.8 |
| Porosity, $P$ (%)[c] | 89 | 87 |
| Specific surface area (m$^2$ g$^{-1}$)[d] | 353 | 76 |
| Carbon/hydrogen content (mass %) | 9.3/1.4 | 5.8/0.6 |
| Appearance | Bluish-transparent | Black |

[a] Calculated from weight and volume.
[b] Measured by helium-pycnometry.
[c] Calculated from bulk density and skeletal density as $P = 100(1 - \rho_{bulk}/\rho_{skel})$.
[d] According to BET measurements.



Figure 1 (——) Thermogravimetric analysis (TG) and (– – –) differential thermal analysis (DTA) of lead titanate aerogels dried from (a) supercritical carbon dioxide and (b) isopropanol. The experiments were performed under a dry air atmosphere with heating rates of 10 K min$^{-1}$.

dioxide, a sharp exothermal signal in this temperature region indicates the phase transition from the amorphous state to crystalline $PbTiO_3$, as reported previously [8]. The broadening of the signal observed in this work indicates a slower crystallization process.

For the sample dried from isopropanol, a total weight loss of only 6% is observed (Fig. 1b); DTA shows the same pattern as for the $CO_2$-dried aerogel. While up to 200 °C a steady mass loss of 0.5% is indicated, the mass increases above 200 °C and almost reaches its initial value at 250 °C. The subsequent weight loss of 6% is completed at 400 °C. A slight further increase has to be attributed to an instrumental drift. No significant exothermal peak in the DTA can be observed at higher temperatures.

Because the DTA signals of $CO_2$- and isopropanol-dried samples below 400 °C show the same general features and the difference in C–H content (Table I) cannot account for the observed differences in total thermogravimetric weight loss, it can be concluded that the burnout of organics is superimposed by a reaction that proceeds under mass uptake from the atmosphere, i.e. an oxidation process.

In order to investigate the nature of this reaction of the isopropanol dried aerogels in more detail, TG/DTA experiments were performed under an inert gas atmosphere, the other parameters remaining unchanged (Fig. 2a). A weight loss of only 1% is observed up to 500 °C. The exothermal DTA signals that indicated the decomposition of organic material are absent under an inert atmosphere. At 327 °C, a sharp endothermal peak becomes apparent; the corresponding DSC signal is given in Fig. 2b. Above 500 °C, an additional steady weight loss of 4.6% is detected; this process seems to be incomplete even at 800 °C, the maximum temperature of the experiment.

Because no weight increase but steady mass loss is observed over the whole temperature region, it can be concluded that the oxidative reaction is suppressed. Only a mass loss of 1% is observed below 500 °C because the removal of organics is hindered by the absence of oxygen. The sharp endothermal DTA signal at 327 °C corresponds to the melting point of metallic lead [12]. From the DSC data and the melting enthalpy of lead [12] it can be calculated that 30 mass % of the sample consists of metallic lead, i.e. about half of the total lead content.

It can be concluded that under the reducing conditions applied during supercritical drying of aerogels in isopropanol (organic solvent, 236 °C, $p > 4.76$ MPa), 50% of the lead (II) which was introduced as $Pb(OAc)_2 \cdot 3H_2O$ is reduced to metallic lead. The presence of traces of elemental lead in PZT films and fibres as a consequence of carbothermal reductions was also found and discussed elsewhere [13].

Additional dilatometer measurements were tried on both types of aerogels ($CO_2$ and isopropanol dried) in order to calculate the envelope density as a function of temperature. However, because of their low density and high porosity, the materials were crushed in the dilatometer at temperatures above 300 °C, which corresponds to the pyrolysis of organic surface groups.

## 3.3. X-ray diffraction

X-ray diffraction patterns of samples annealed at different temperatures were taken. PT-aerogels dried from carbon dioxide do not show any crystalline phases up to baking temperatures of 250 °C (Fig. 3a). At 340 °C, reflexes characteristic for litharge ($\alpha$-PbO) and macedonite (tetragonal lead titanate) become apparent. Above 500 °C, macedonite becomes the dominant crystalline phase along with traces of $Pb_2Ti_2O_6$ (pycrochlore) [14, 15] at 30.9° and 34.6° 2$\theta$. The amount of $PbTi_2O_6$ is reduced at higher baking temperatures.
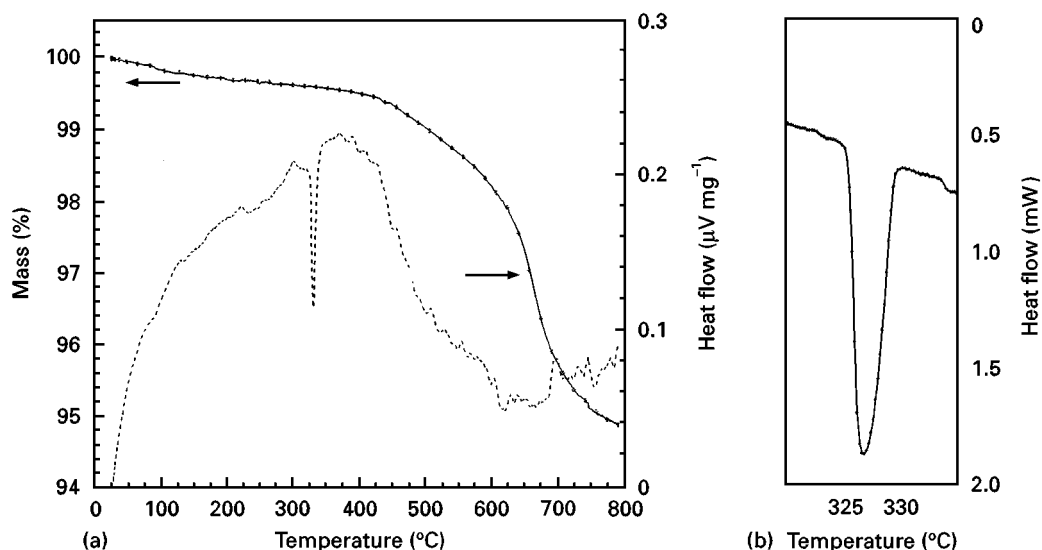


*Figure 2* (a) (——) Thermogravimetric analysis (TG) and (– – –) differential thermal analysis (DTA) and (b) differential scanning calorimetry (DSC) of a lead titanate aerogel dried from supercritical isopropanol. Both measurements were taken under nitrogen atmospheres with heating rates of 10 K min$^{-1}$. The endothermal signals at 327 °C indicate the melting of metallic lead.
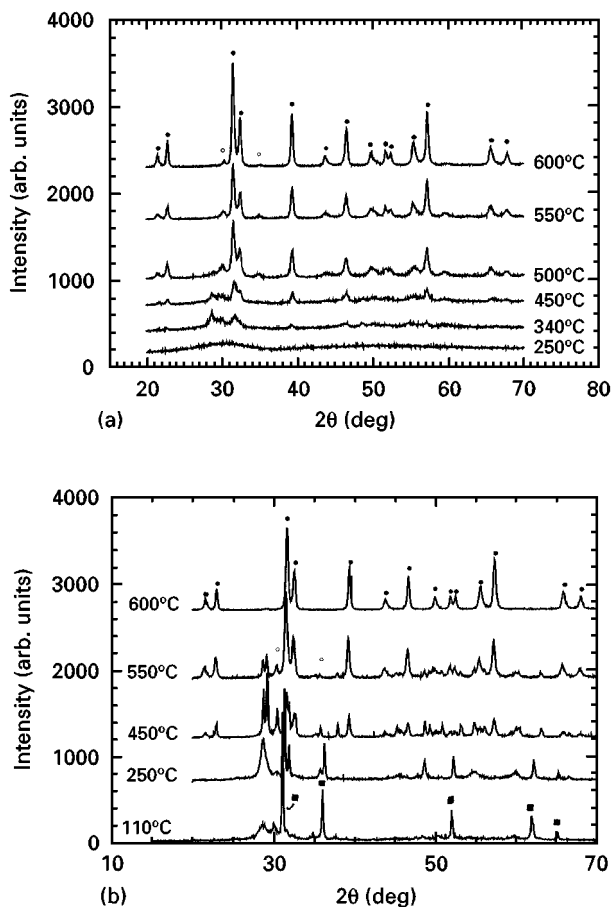
*Figure 3* X-ray diffraction pattern of lead titanate aerogels dried from (a) supercritical carbon dioxide and (b) isopropanol after annealing at the indicated temperatures for 1 h. Typical reflexes identified from PDF-files are marked as (●) macedonite-PbTiO₃, (○) pyrochlore, Pb₂Ti₂O₆, and (■) metallic lead, Pb. For intermediate annealing temperatures (340–550 °C), complex mixtures of lead oxides are present.

Based on the XRD data at hand, no decision can be made whether lead oxide and lead titanate evolve concurrently from the amorphous materials or if PbO is the intermediate phase. It should be noted, however, that the onset of crystallization to tetragonal PbTiO₃ is observed at significantly lower temperatures compared with samples from other synthesis routes [8], where the lead titanate aerogels dried from supercritical carbon dioxide showed a direct phase transition from the amorphous state to pure crystalline PbTiO₃ between 450 and 500 °C.

From the XRD measurements there is no evidence for a crystalline titanium-rich intermediate phase. Thus, it can be concluded that the crystallization proceeds continuously initiated by PbO or PbTiO₃ seeds under consumption of the amorphous material. This model is supported by the broad exothermal DTA signal at 510 °C (Fig. 1a).

In contrast to PT-aerogels investigated previously [8], the formation of pyrochlore (Pb₂Ti₂O₆) is observed. At 600 °C only traces of this crystalline, non-piezoelectric material are detected from the corresponding XRD signal intensities. Even though the new synthesis route offers the advantage of an earlier crystallization onset, higher temperatures have to be applied to remove undesired secondary phases.

Aerogels dried from isopropanol (Fig. 3b) show the sharp diffraction pattern of elemental lead, which is also the cause of the black appearance of the material (Table I) and confirms the conclusions drawn from the thermal analysis of these samples. Additional reflexes probably indicate the presence of lead-oxo carbonates. The broadness and low intensity of the peaks precludes unambiguous identification, however. Such phases would result as intermediates from the partial pyrolysis of lead acetate.

At 250 °C, litharge (α-PbO) crystallizes and the intensity of the reflexes attributed to metallic lead decreases. This shows that oxidation of lead is initiated in this temperature region. Metallic lead can no longer be detected in aerogels treated at 450 °C, where litharge (α-PbO) and massicot (β-PbO) coexist with macedonite (tetragonal lead titanate). The peak intensities of the lead oxides are diminished at 550 °C and only PbTiO₃ is detectable in samples treated at 600 °C. No traces of pyrochlore are found.

Homogeneity of materials on a molecular level is often stated as an advantage of sol–gel processing [15]. In the present case of the lead titanate aerogels dried from supercritical isopropanol, extensive phase separation does occur, but this synthesis route can still be applied successfully for the preparation of highly porous PbTiO₃ ceramics.

## 3.4. Transmission electron microscopy

Investigations of lead titanate aerogels dried from carbon dioxide do not reveal any information additional to that of our previous studies [7,8], even though a different synthesis route was applied; the material consists of globular primary particles which are arranged in irregular clusters.

However, the aerogels dried from supercritical isopropanol show completely different features (Fig. 4a). Along with high-contrast globular particles (diameter 26 ± 5 nm), fine needles are present. The interwoven needles are up to 150 nm long with diameters between 7 and 10 nm. Dark-field images show that these structures are crystalline. Because metallic lead is not expected to crystallize in the form of needles, these are believed to be either the lead-oxo carbonates inferred from the XRD data (Fig. 3b) or crystalline TiO₂ (rutile). The latter species may not show up in the X-ray diffraction pattern because of the high absorbance coefficient of metallic lead also present in the sample.

Upon annealing at 600 °C the microstructure is completely altered (Fig. 4b); there is now a network of particles with diameters between 25 and 35 nm. The particles are interconnected by strings which are also crystalline. Dark-field images reveal that monocrystalline orientation is maintained over neighbouring particles. In these samples, only tetragonal PbTiO₃ was detected by X-ray diffraction (Fig. 2b). A general feature of the aerogels treated at 600 °C compared to earlier investigations [8] is that the grain growth and final morphology seem to be influenced by the crystalline needle-like structures present at intermediate heating stages.
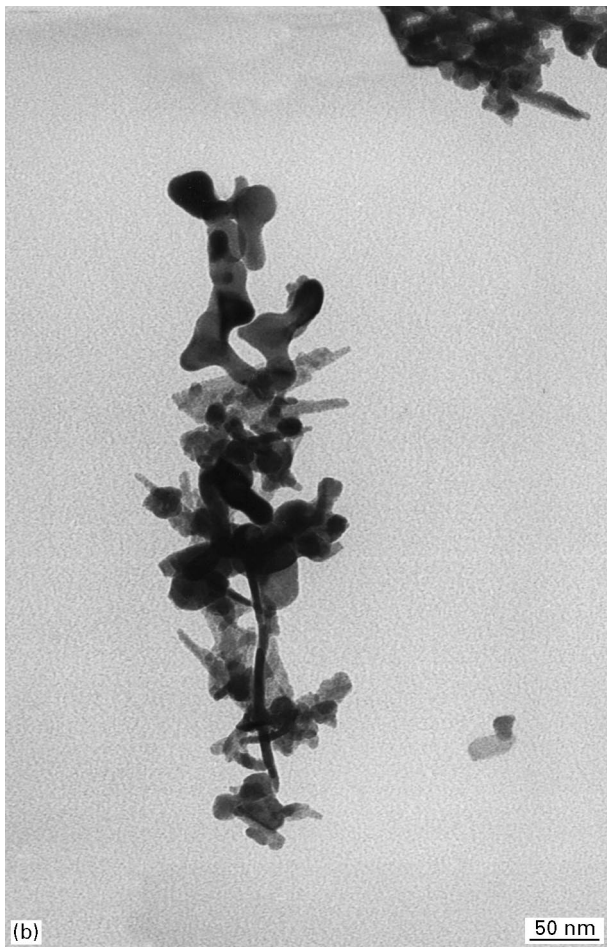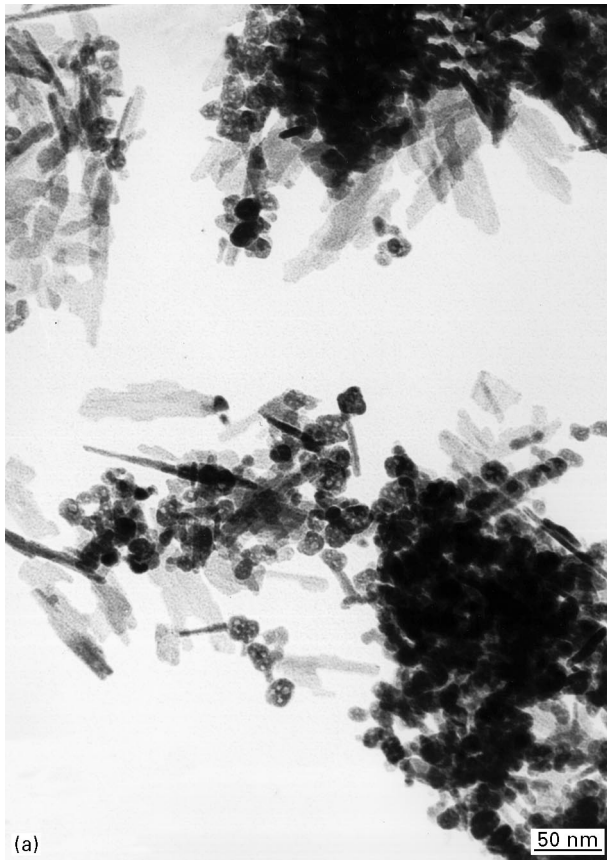
(a)
50 nm



(b)
50 nm

*Figure 4* Transmission electron micrographs taken from lead titanate aerogels dried in supercritical isopropanol. The untreated sample (a) contains fine crystalline needles along with globular particles. Aerogels annealed at 600 °C for 7 h exhibit crystalline grains (b) which are connected by elongated strings.

## 3.5. Helium pycnometry

The skeletal density of PT-aerogels cured at different temperatures was measured by helium pycnometry (Fig. 5). Starting with an initial skeletal density of $3.7 \, \text{g cm}^{-3}$, aerogels dried from supercritical carbon dioxide reach the theoretical density of crystalline $PbTiO_3$ ($7.52 \, \text{g cm}^{-3}$) after heat treatment at 600 °C for 1 h. Between 250 and 300 °C a steep increase in skeletal density is observed.

Aerogels obtained from supercritical isopropanol exhibit an initial skeletal density of $4.8 \, \text{g cm}^{-3}$, but their increase in density to $7.5 \, \text{g cm}^{-3}$ is almost linear. No significant steps in the plot can be detected. For annealing temperatures above 300 °C the evolution of skeletal densities for both types of aerogel is very similar, a maximum deviation of $0.3 \, \text{g cm}^{-3}$ being observed.

The skeletal density of the amorphous $CO_2$-dried samples is significantly lower than that of the partially crystalline material obtained from isopropanol (Table I, Fig. 5). After firing at temperatures above 300 °C both types of aerogel contain lead oxides and thus exhibit about the same skeletal density. The theoretical density of tetragonal $PbTiO_3$ is reached at 600 °C; this result is in agreement with the X-ray diffraction experiments (Fig. 2a and b), because this phase is dominant at 600 °C.

We previously demonstrated that skeletal densification is the main reason for the shrinkage of $CO_2$-dried lead titanate aerogels before crystallization [8]. Strong skeletal densification due to the oxidative decomposition of organics and the onset of crystallization between 250 and 300 °C is believed to be responsible for the cracking of the $CO_2$-dried materials investigated in this study.

Lead titanate aerogels dried in supercritical isopropanol exhibit a higher initial skeletal density. We assume that the smooth and steady increase in skeletal density towards the theoretical density of $PbTiO_3$ reduces internal stresses within the aerogel and thus cracking can be avoided.
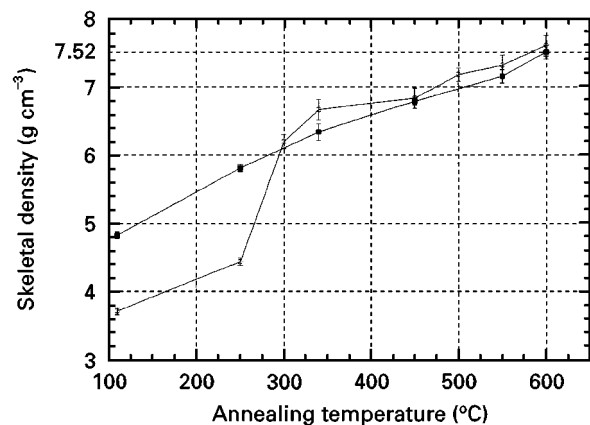


*Figure 5* Skeletal densities of lead titanate aerogels as a function of annealing temperature measured by helium-pycnometry. Whereas material dried from supercritical isopropanol (—■—) is densified almost linearly, the skeletal density of $CO_2$-dried aerogels (——○——) exhibits a steep increase between 250 and 300 °C. Both types of material reach the theoretical density of tetragonal $PbTiO_3$ at 600 °C.

## 3.6. Nitrogen adsorption experiments

The specific surface area of aerogels annealed at temperatures between 110 and 600 °C was determined by nitrogen adsorption experiments. The results according to BET theory are given in Fig. 6. For $CO_2$-dried samples that had only undergone the heat treatment necessary for sample preparation (110 °C), a specific surface area of 353 $m^2 g^{-1}$ is measured. This value is drastically reduced to 65 $m^2 g^{-1}$ upon annealing at 300 °C for 1 h; from this point the specific surface area steadily decreases to 14 $m^2 g^{-1}$ at 600 °C. This behaviour supports the interpretation that the transition from the yet amorphous state to a material with crystalline regions is associated with ripening phenomena and strong particle growth.

Isopropanol-dried aerogels treated at 250 °C show a surface area of 86 $m^2 g^{-1}$ compared to 76 $m^2 g^{-1}$ for uncured materials. Higher baking temperatures up to 600 °C reduce the specific surface area in a similar fashion to that observed for materials dried from carbon dioxide.

Above 300 °C, the specific surface areas determined for aerogels dried in carbon dioxide and isopropanol show the same behaviour; the values steadily decrease. Even though the results of helium-pycnometry and BET surface measurements are similar between 300 and 600 °C, one should not take this as evidence of identical microstructure. Nevertheless, it is obvious that the changes that occur up to 300 °C are more pronounced for lead titanate aerogels dried in $CO_2$. This is supposed to be a major reason why this type of aerogel cannot be transformed to highly porous monoliths.

## 3.7. Preparation of crystalline monolithic PbTiO$_3$-aerogels

Thin slices of PT-aerogels dried in supercritical isopropanol were annealed at 600 °C for 1 h in a preheated furnace. The envelope density of these samples is 0.75 $g cm^{-3}$ as determined by weight and volume. With a skeletal density of 7.5 $g cm^{-3}$, a porosity of
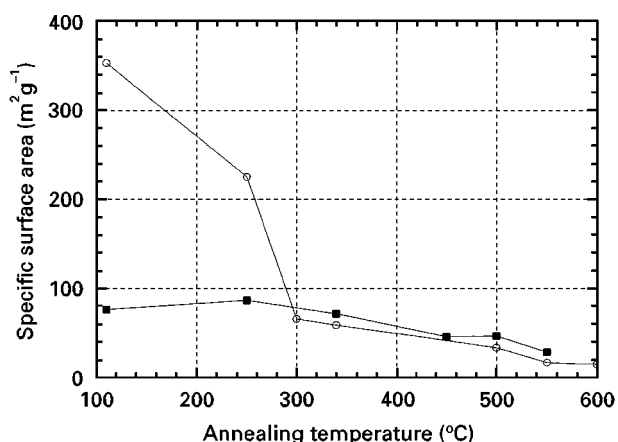
*Figure 6* Specific surface area (BET method) as a function of annealing temperature. Aerogels obtained from supercritical isopropanol (———■———) show a small and steady decrease in specific surface area compared to $CO_2$-dried material (———○———).
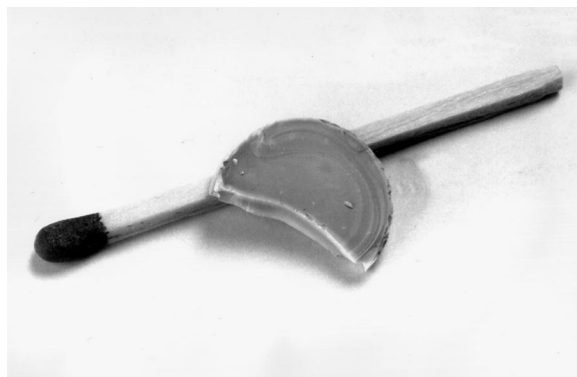
*Figure 7* Photograph of a monolithic crystalline lead titanate aerogel-disc together with a match as scale.

90% can be calculated. A photograph of a typical aerogel slice is given in Fig. 7. Even though the material is very brittle, it can be handled without problems. In order to decrease the probability of cracking during the heat treatment, heating rates of 0.5 K $min^{-1}$ were applied with a holding time of 1 h at the final temperature of 600 °C. Such monolithic PT-aerogels could not be obtained from material dried in carbon dioxide even under these gentle annealing conditions.

## 4. Conclusion

Different supercritical drying conditions have been applied to lead titanate gels derived from a sol–gel process. The resulting aerogels and their thermal behaviour are compared: the material derived from supercritical carbon dioxide is amorphous after drying; upon heat treatment and the removal of residual organics the network is continuously transformed to tetragonal lead titanate in the temperature range 340–600 °C. Up to 300 °C a strong densification of the inorganic aerogel backbone takes place, which leads to the disintegration of the material.

When the lead titanate gels under investigation were dried in supercritical isopropanol, carbothermal reduction took place. The resulting material contains considerable amounts of metallic lead. Upon firing in air, the lead is oxidized to a complex composition of lead oxides that reacts continuously to tetragonal PbTiO$_3$. The skeletal densification associated with the firing process is steady; therefore the material remains monolithic.

At first sight, the observed phase separation during supercritical drying seems to be a disadvantage, because the homogeneity on the molecular level, that is often stated as a major advantage of sol–gel processing, is lost during this step. Nevertheless, the early densification of the material and the continuous phase transformations allow the crystallization to monolithic PbTiO$_3$ aerogels without cracking.

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