

Structural Study of the Formation of Lead Zirconate Titanate via Sol-Gel Process

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Abstract

The structures of the precursors $Zr(OPr^n)_4$ and $Ti(OPr^n)_4$ in solution were investigated by means of NMR and IR spectroscopy and, in the case of $Zr(OPr^n)_4$, by means of EXAFS spectroscopy. The results were confirmed by gel permeation chromatography, which reveals dimers on average. Following chemical modification of the precursors with acetic acid, their degree of association was unaltered. Hydrolysis and condensation reactions were controlled by esterification of propanol with acetic acid and accompanied by the growth of oligomers, presumably by the Ostwald ripening mechanism. The reaction of the chemically modified precursors with $Pb(OAc)_2$ results, after calcining, in the formation of lead zirconate titanate (PZT). Addition of water to the sol immediately or after three weeks, led to different products. Large angle X-ray diffraction showed that ageing of the sol favours the formation of lead zirconate titanate and results in higher crystallinity.

Introduction

In comparison with the conventional powder route, sol-gel processing of lead zirconate titanate powder offers several advantages, such as low calcination and sintering temperatures, better control of chemical composition, and mixing of the components in the liquid state [1 - 6]. The properties of the product are

a result of the molecular to colloidal-scale structures that form during mixing of the components, ageing, gelation, drying, and calcining. In order to deduce these relationships, we studied the structures of the precursors. The evolution of PZT during sol-gel process and calcination was investigated with a variety of spectroscopic and analytical methods.

For the synthesis of lead zirconate titanate we found a suitable model system, which starts with the educts lead acetate, zirconium and titanium n-propoxide. The remarkable feature of this system is the occurrence of all reactions important in a sol-gel process, such as chemical modification of precursors, hydrolysis and condensation.

Experimental

Zirconium n-propoxide was purchased from Hüls AG, titanium n-propoxide, acetic acid, and lead acetate from Aldrich-Chemie GmbH & Co. KG. The alkoxides were distilled and handled under dry nitrogen. To produce the complexes, each propoxide was mixed with acetic acid at room temperature (molar ratio $\text{Zr}(\text{nOPr})_4 : \text{HOAc} = 1 : 2$ and $\text{Ti}(\text{nOPr})_4 : \text{HOAc} = 1 : 1$). For preparation of PZT, acetic acid was added to a mixture of zirconium and titanium n-propoxides (molar ratio $\text{Zr} : \text{Ti} = 0.45 : 0.55$) in the molar ratio $\text{HOAc} : \text{Ti} + \text{Zr} = 1.5 : 1$. The solution was added dropwise to lead acetate dissolved in methanol at 65°C . After the mixing of the components two different routes were followed. The first involved hydrolysis of the solution after three weeks by addition of water in the molar ratio $\text{H}_2\text{O} : (\text{Ti} + \text{Zr}) = 18 : 1$, in the second route the hydrolysis was performed immediately after mixing the components. All gels were dried at 130°C and calcined at different temperatures up to 600°C (Fig. 1).

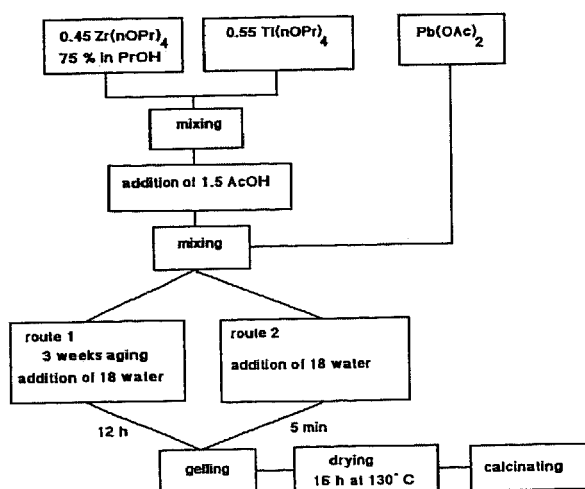


Fig. 1 Overview of the synthesis of lead zirconate titanate by a sol-gel process

Results and discussion

1) Structure of the precursors dissolved in the parent alcohol

An important factor that influences reaction kinetics and the resulting structures is the extent of oligomerization of the precursors. We determined the average degree of association by vapour pressure osmometry and gel permeation chromatography (calibrated with polymethylsiloxanes). Both methods showed the existence of dimers. To elucidate the structure of $Zr(OPr^n)_4$ in solution, we performed EXAFS experiments on the Zr K-edge at DESY, Hamburg. The data evaluation and interpretation will be described in detail elsewhere. Only the results are given here (Fig 2).

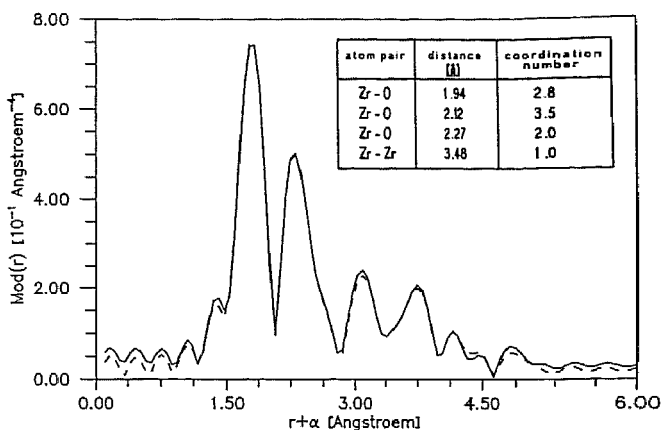


Fig. 2 Fourier transform of the experimental (solid line) and simulated (dotted line) Zr K-edge EXAFS spectrum of $Zr(OPr^n)_4$, dissolved in propanol, and interatomic distances and coordination numbers

They are consistent with dimers composed of bridging and terminal n-OPr ligands (Fig. 3).

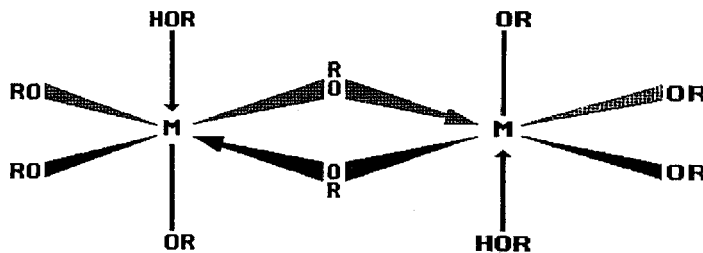


Fig. 3 Proposed structures of $Ti(OPr^n)_4$ and $Zr(OPr^n)_4$, dissolved in propanol (M = Ti, Zr)

Since EXAFS spectroscopic measurements at the Ti K-edge could not be performed, the structure of $\text{Ti}(\text{OPr}^n)_4$ in solution was characterized with dynamic ^1H NMR spectroscopy. The spectra show that alcohol exchanges very readily, but at -60°C both terminal and bridging O-Pr-groups are present, a fact which indicates at least a dimeric structure. This result is in agreement with other studies [7,8].

2) Chemical modification of the precursors

Hydrolysis of a mixture $\text{Zr}(\text{OPr}^n)_4$ and $\text{Ti}(\text{OPr}^n)_4$ results in a precipitate, whereas homogeneous gels can be obtained after treatment of the precursors with acetic acid. The addition of acetic acid causes an exothermic reaction.

It was shown by potentiometric titration and by IR spectroscopy that the mono-acetate was formed in the reaction of $\text{Ti}(\text{OPr}^n)_4$ with acetic acid. Gel permeation chromatography indicated an unaltered degree of association. The infrared spectrum of the product exhibits two strong bands at 1450 cm^{-1} and 1550 cm^{-1} , which can be assigned to the symmetric and antisymmetric stretching vibrations of the carboxylic group with a frequency difference of 100 cm^{-1} , typical of an acetate acting as a bidentate ligand [9]. We propose a dimer structure of AcOH-modified $\text{Ti}(\text{OPr}^n)_4$ (Fig. 4).

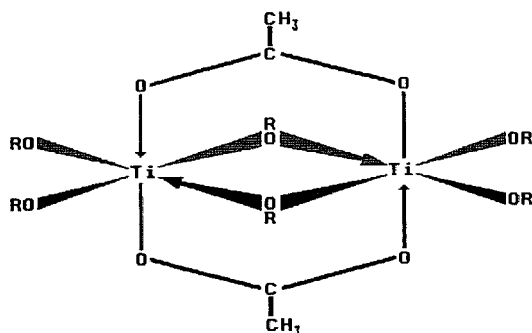


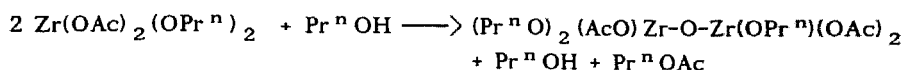
Fig. 4 Probable structures of AcOH-modified $\text{Ti}(\text{OPr}^n)_4$

In contrast to $\text{Ti}(\text{OPr}^n)_4$, two alkoxy groups are substituted in the reaction of $\text{Zr}(\text{OPr}^n)_4$ with acetic acid. The spectroscopic and analytical methods mentioned above, and, in addition, EXAFS spectroscopy at the Zr K-edge indicate an unaltered degree of oligomerization with acetic acid acting as chelating ligand, as well as the existence of bridging and terminal OPr^n ligands.

3) Condensation of HOAc-modified $\text{Zr}(\text{OPr}^n)_4$ and $\text{Ti}(\text{OPr}^n)_4$

In order to elucidate the influence of ageing on the modified precursors, we prepared a solution of $\text{Zr}(\text{OAc})_2(\text{OPr}^n)_2$ in propanol and studied, by means of IR and ^1H NMR spectroscopy, the evolution of the structures over three weeks.

These studies showed a transesterification, very similar to a reaction found by Sanchez et al. [9], according to:



Gel permeation chromatography showed this reaction to be accompanied by an increase in the degree of polymerization. After three weeks a gel formed; a molecular weight of 100 000, relative to Polydimethylsiloxanes, was then found.

In contrast, $\text{Ti}(\text{OAc})(\text{OPr}^n)_3$ did not show this effect. Although the transesterification could be observed - in a somewhat slower reaction, than the one observed for $\text{Zr}(\text{OAc})_2 (\text{OPr}^n)_2$ - only oligomers were found and no formation of a gel could be detected. The lower reactivity may explain the low degree of polymerization. It should be noted, however, that in $\text{Ti}(\text{OAc})(\text{OPr}^n)_3$ only one acetyl group can act as a leaving group in the condensation reaction. Since $\text{Zr}(\text{OAc})_2 (\text{OPr}^n)_2$ has two acetyl groups, the formation of networks may be more favourable for zirconium than for titanium.

4) Formation of lead zirconate titanate sol and ageing in absence of water

The lead zirconate titanate sol was prepared as described in the experimental section, without addition of water (route 2). The transesterification of acetic acid started the condensation reactions and led to a growth of the particle size, whose evolution was studied by gel permeation chromatography. Immediately after the mixing of the components, two peaks at 140 and 1550 relative molecular weight were observed. After six days a weight-average of 71 000 could be detected. After 12 days the sol contained polymer species with a molecular weight of 285 000 and a particle size of 1.1 nm, which was determined by dynamic light scattering. After 60 days larger particles with a diameter of 4.5 nm were formed, thereby consuming smaller particles. This phenomenon is well known in the literature and is called Ostwald ripening [10].

In order to elucidate the structure of the sol, we performed EXAFS experiments. The analysis of the EXAFS spectra at the Zr K-edge revealed two different Zr-O-pairs and one Zr-Ti pair (Fig. 5). Since a better understanding of the sol-gel process requires information on whether an inorganic network, similar to the structure of lead zirconate titanate, is already formed during the sol-gel process, we analyzed the data very carefully. The backscattering atom could be unambiguously identified from the experimentally determined amplitude and phase of the separated peak and from fitting routines. Efforts to fit our data with other types of backscatterers, such as Zr or Pb, failed.

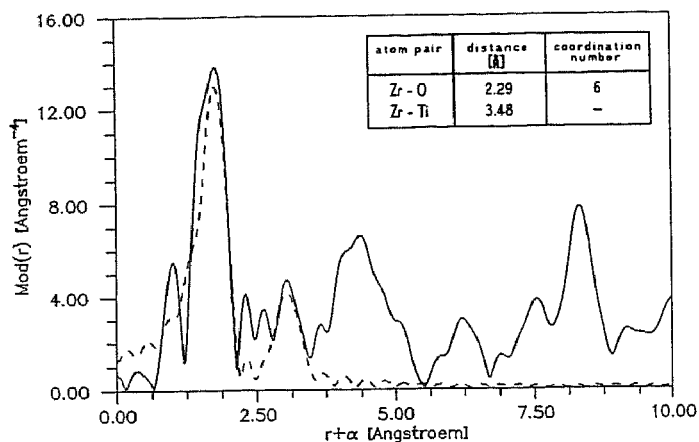


Fig. 5 Fourier transform of the experimental (solid line) and simulated (dotted line) Zr K-edge EXAFS spectrum of the sol and interatomic distances and coordination numbers

5) Structure of lead zirconate titanate gel after addition of water

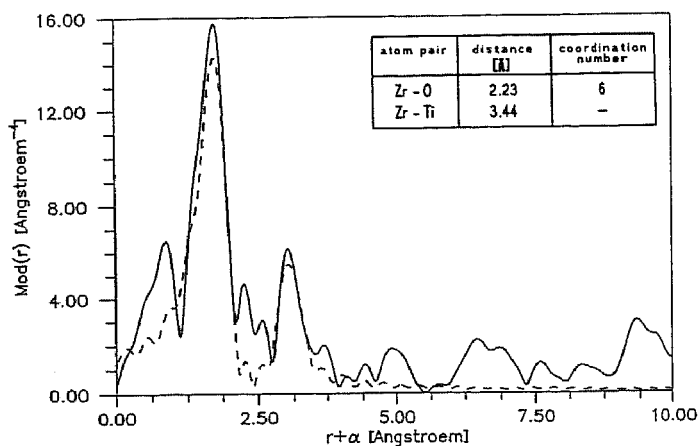


Fig. 6 Fourier transform of the experimental (solid line) and simulated (dotted line) Zr K-edge EXAFS spectrum of the gel and interatomic distances and coordination numbers

The gel was prepared from the sol by ageing at room temperature for three weeks

and by addition of water in the molar ratio given in the experimental section (route 1). The structure of the gel obtained after 12 hours was determined by means of EXAFS spectroscopy. The interpretation of the EXAFS spectra at the Zr K-edge confirms the results obtained for the sol. The fact that the interatomic distances are significantly shorter reflects the higher density of the gel compared to the sol.

6) Calcination of the lead zirconate titanate gels

The evolution of the degree of crystalline order and particle size of the gel during the calcination process were studied by means of large angle X-ray diffraction. Fig. (7) shows the X-ray diffraction patterns of gels prepared via route 1 and 2, respectively, as a function of the temperature of calcination. The gel was dried at 120°C, the other samples were calcined for 4 hours at the temperatures shown on the left hand side of the figures.

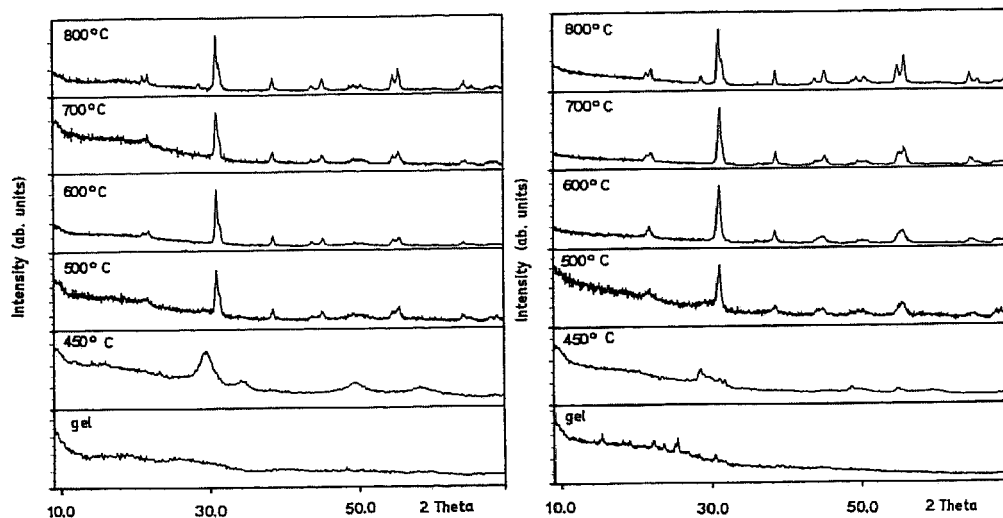


Fig. 7 Large angle X-ray scattering intensities of lead zirconate titanate gel, prepared via route 1 (left hand side) and route 2 (right hand side), as a function of the temperature of calcination

The X-ray intensities of the gel prepared by rapid hydrolysis show small Bragg reflexes. These can be identified, by comparison with reference samples, as TiO_2 and ZrO_2 . The occurrence of such microcrystalline components indicates that the hydrolysis is very similar to coprecipitation. In contrast, microcrystalline phases

are absent in the aged gel. The ageing of the sol also results in higher crystallinity.

The formation of lead zirconate titanate started at 500 °C and was completed at 600 °C. The particle size, determined from the sharpness of the Bragg reflexes, increased with increasing temperature of calcination.

Conclusion

A sol-gel process for the preparation of PZT out of lead acetate, zirconium n-propoxide and titanium n-propoxide, modified with acetic acid, is described. The structures of the modified precursors and their degree of polymerisation during ageing had great influence on the PZT formation. Ageing of the sol favours the development of the ceramic, which can be achieved at lower temperatures and with higher crystallinity than with a fresh sol.

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Acknowledgements

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