

First Evidence of the Preformation of an Inorganic Network in Sol-Gel Processing of Lead Zirconate Titanate, obtained by EXAFS Spectroscopy

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We report the results of EXAFS spectroscopical investigations on lead zirconium titanium precursors in the sol and gel state. Analysis of the second coordination shell for both the sol and the gel yields the contribution of titanium backscatterers at a mean distance of 3.48 Å (sol) and 3.44 Å (gel). We draw the conclusion that a uniform composition on a microscopic scale exists in the sol as well as the gel state. In other words, heterocondensation is favoured against homocondensation. This provides a good explanation of the low calcination and sintering temperatures in the sol-gel processing of lead zirconate titanate compared with other preparation techniques.

Sol-gel processing of lead zirconate titanate has some advantages compared with other preparation techniques, in terms of lower calcination and sintering temperatures, better control of chemical composition and mixing of components in the liquid state [1–6]. Over the last few years we have developed and investigated a synthesis of lead zirconate titanate via the metal alkoxide route, which will be described in detail elsewhere [7]. In this paper we attempt to answer the question, which type of metal linkage exists in the sol and gel. Two extreme cases are possible: The metal alkoxides condense with themselves (homocondensation) or with the other metal component (heterocondensation). In the first case a product, similar to a coprecipitate of hydrous oxide, is formed; in the second case a mixture on the molecular scale is obtained. Its homogeneity favours the conversion to lead zirconate titanate and should provide a good explanation of the low calcination and sintering temperatures.

In order to decide whether constituent parts of the inorganic network of crystalline lead zirconate titanate are already formed in the condensation process, we tried to elucidate the type of metal-oxygen-metal linkage in the sol and gel. This analysis cannot be easily achieved with conventional spectroscopic methods. EXAFS spectroscopy, however, is a powerful tool for determining the local order in amorphous materials. It provides structural information on the local environment of the absorbing atom.

EXAFS spectra of lead zirconium titanium precursors in the sol and gel state and crystalline PZT were measured in transmission mode at the Hamburger Synchrotronstrahlungslabor (HASYLAB) using the synchrotron radiation from the DORIS storage ring and the beam line RÖMO II. To avoid problems with the morphotropic phase boundary we investigated a precursor system that yields a chemical composition of $\text{PbZr}_{0.45}\text{Ti}_{0.55}\text{O}_3$ after calcination. The crystalline PZT was prepared by the conventional mixed oxide method. The sol was prepared by adding the metal n-propoxides (molar ratio $\text{Zr}:\text{Ti} = 0.45:0.55$) in the parent alcohol and acetic acid (molar ratio $\text{Ac}:(\text{Zr}/\text{Ti}) = 1.5:1$) to a stirred solution of lead acetate in methanol at 65°C . Hydrolysis of the sol by adding water (molar ratio $\text{H}_2\text{O}:(\text{Ti}/\text{Zr}) = 18:1$) three weeks after mixing the components yields the gel [7]. The structure of the gel obtained after 12 hours was determined by means of EXAFS spectroscopy.

A summary of theoretical relations is found in [8–9]. Data reduction of the experimental EXAFS spectra involving conversion of the raw data, energy calibration, background removal, normalisation and Fourier-filtering is described in detail in [10]. The main problem of the data reduction is caused by the high static disorder of amorphous substances, resulting in low-amplitude EXAFS oscillations. The usual method of removing the background is to fit the modulation of the absorption coefficient with a polynomial spline of defined order over the total range, or of different

orders over a series of equidistant intervals. Since this method fails mostly, when applied to spectra of amorphous systems, we used a modified smoothing-spline algorithm [10–12].

EXAFS spectra were evaluated in the range of 18.026 eV to 18.548 eV (corresponding to: 2.72 \AA^{-1} to 12.0 \AA^{-1} in k space) for the sol and 18.029 eV to 18.548 eV (corresponding to: 2.86 \AA^{-1} to 12.0 \AA^{-1} in k space) for the gel, weighted by k^3 and Fourier transformed with a square window. The radial distribution functions of the sol and gel were back-transformed in the ranges of 1.20 \AA to 3.44 \AA (sol), and 1.12 \AA to 3.54 \AA (gel), respectively, into k space with a square window. The Fourier-filtered $\chi(k)$ functions agree with the experimentally determined $\chi(k)$ functions.

Curve fitting of the $\chi(k)$ functions reveals that the first coordination shell consists of 6 oxygen atoms, which are connected directly to the zirconium atom, at a mean distance of $r = 2.29 \text{ \AA}$ (sol) and $r = 2.23 \text{ \AA}$ (gel). This result is confirmed by the asymmetry of the first peaks of the Fourier-transform of the experimental $\chi(k)$ functions, which indicate two different types of Zr–O-pairs (Fig. 1). The significantly shorter Zr–O distance in the gel reflects the higher density of the gel compared with the sol. The coordination number

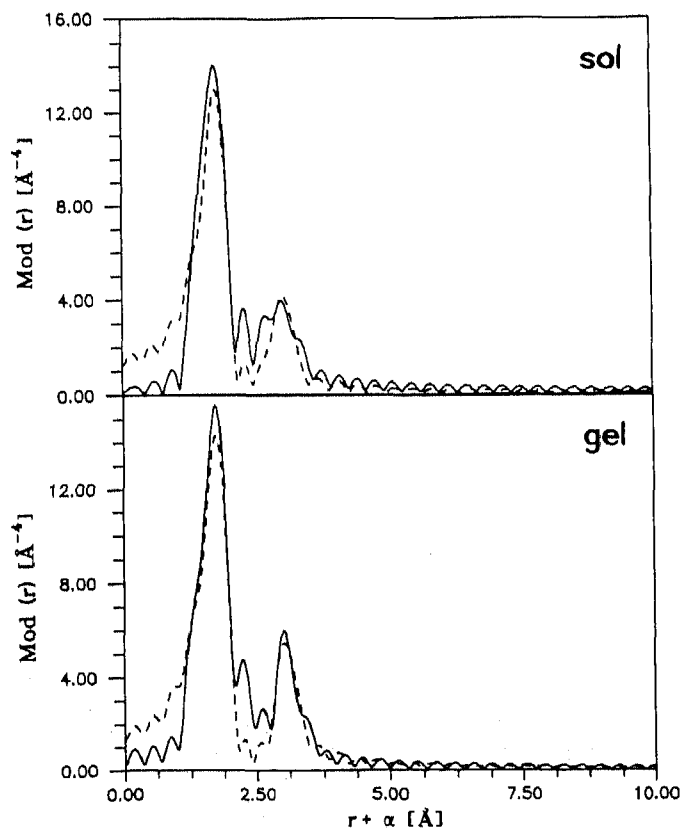


Fig. 1 Fourier transform of the Fourier filtered experimental (solid line) and simulated (dashed line) Zr K-edge EXAFS spectrum of the sol and gel

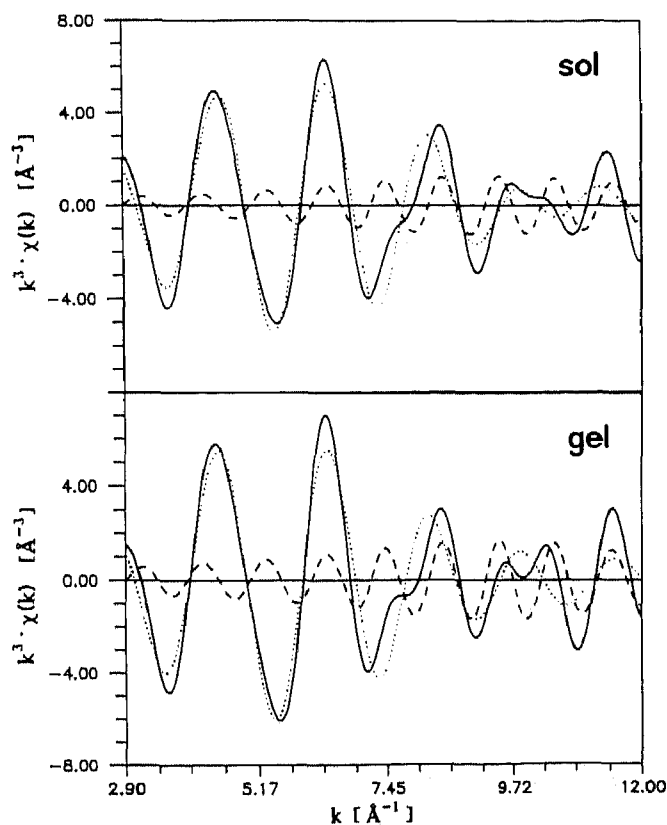


Fig. 2 Fourier filtered $k^3 \cdot \chi(k)$ functions of the Zr K-edge EXAFS spectrum of the sol and the gel. (Range of filtering of radial distribution function, Sol: $1.20 \text{ \AA} - 3.44 \text{ \AA}$ (solid line), $1.20 \text{ \AA} - 2.10 \text{ \AA}$ (dotted line), $2.80 \text{ \AA} - 3.40 \text{ \AA}$ (dashed line); Gel: $1.12 \text{ \AA} - 3.54 \text{ \AA}$ (solid line), $1.12 \text{ \AA} - 2.10 \text{ \AA}$ (dotted line), $2.75 \text{ \AA} - 3.54 \text{ \AA}$ (dashed line))

of the first shell was rescaled with the corresponding value, obtained from the EXAFS spectrum of crystalline PZT, where the coordination number of Ti or Zr is six.

Curve fitting of the second coordination shell shows similar agreement of the fitted and Fourier-filtered $\chi(k)$ functions with zirconium or titanium as backscattering atom. Significant differences between the fitted and experimental calibration energies for zirconium (16.2 eV sol and 19.3 eV gel) and small differences for titanium (= 3.3 eV sol and

–2.5 eV gel) indicate that zirconium as backscattering atom of the second shell is not a good model for the filtered $\chi(k)$ functions. Assumption of additional coordination shells improves the agreement with the experimentally determined $\chi(k)$ function, but reduces the reliability of the results.

Backtransformation of the pseudoradial distribution function in the range of 2.80 Å to 3.40 Å (sol) and 2.75 Å to 3.54 Å (gel) into k space (Fig. 2) provides the contribution of the second coordination shell. In order to furnish a proof

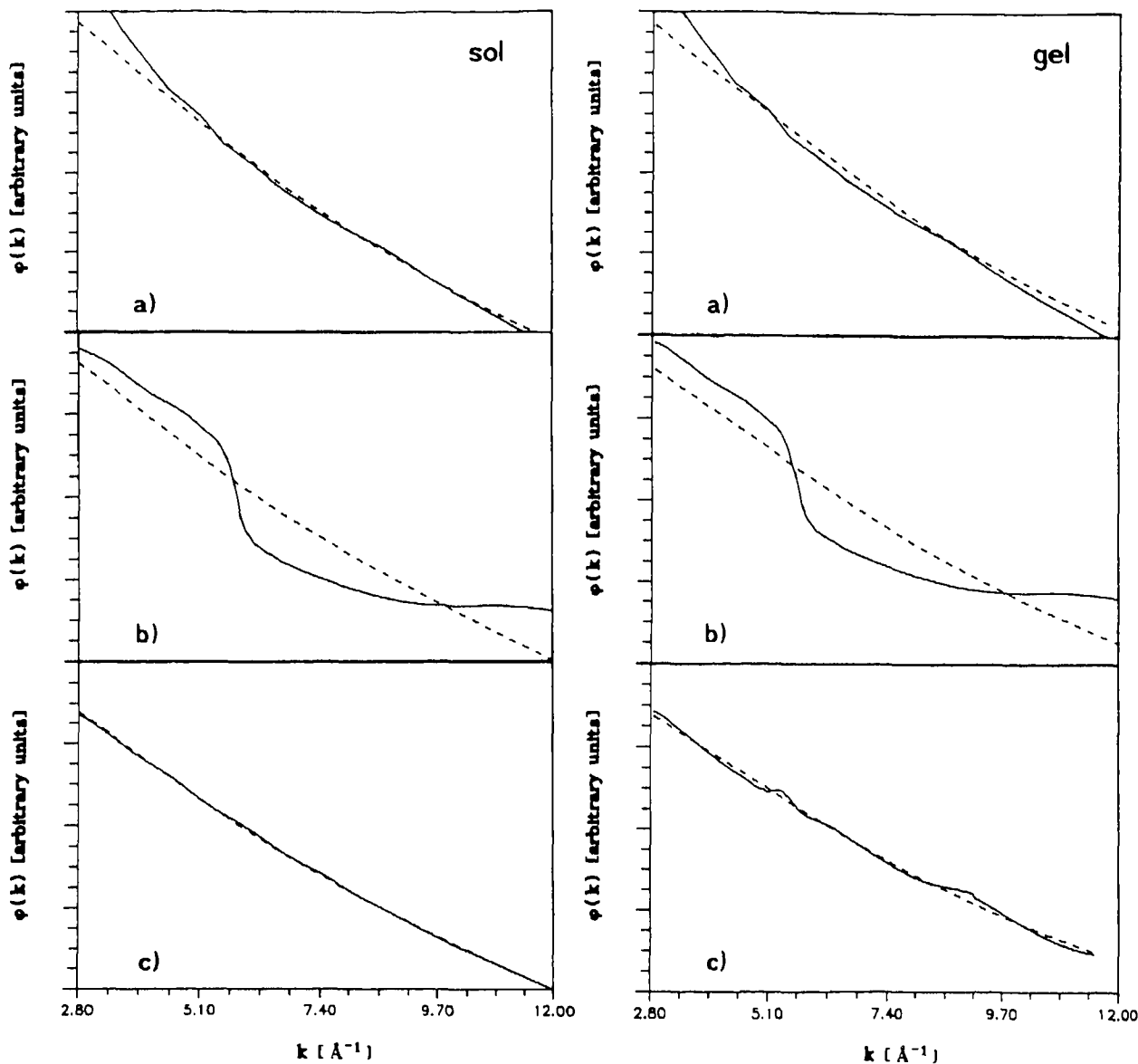


Fig. 3

Experimentally determined phase functions for the second coordination shells of the sol and the gel (dashed line) compared with the values computed by McKale [13] (solid line).

(It should be noted, that the phase functions were adjusted to the data of McKale [13] by variation of the shift of the threshold energy ΔE and the absorber-backscatterer distance r . Therefore the results differ slightly from those obtained by curve fitting of both coordination shells.)

sol: a) backscatterer: zirconium; ($\Delta E = 16.20$ eV, $r = 3.55$ Å).

b) backscatterer: lead; ($\Delta E = 2.85$ eV, $r = 3.51$ Å).

c) backscatterer: titanium; ($\Delta E = 8.55$ eV, $r = 3.48$ Å).

gel: a) backscatterer: zirconium; ($\Delta E = 19.30$ eV, $r = 3.54$ Å).

b) backscatterer: lead; ($\Delta E = 8.55$ eV, $r = 3.49$ Å).

c) backscatterer: titanium; ($\Delta E = 9.0$ eV, $r = 3.44$ Å).

from the existence of Zr–O–Ti linkages, the phase function of the second shell was compared with those tabulated by McKale [13]. From the experimentally determined phase (Fig. 3) the backscattering atom of the second shell could be unambiguously identified as titanium. To confirm this result, all possible species of atoms were tested as backscatterer; titanium, however, showed the best agreement of the theoretically and experimentally determined phases, of the fitted and filtered $\chi(k)$ functions and low differences between the fitted and experimental calibration energies.

From the fits a Zr–Ti mean distance of $r = 3.48 \text{ \AA}$ (sol) and $r = 3.44 \text{ \AA}$ (gel) was deduced. Assuming a Ti–O distance of 1.94 \AA as in rutile (TiO_2) [14] we calculated a Zr–O–Ti mean angle of 110.5° for the sol and 111.0° for the gel. Because of the inaccuracy of the coordination number, we refrain from giving a value. From the obtained distances and atom pairs we must conclude that there is considerable evidence that the zirconium atom is linked to a titanium atom by two oxo-groups in the form of double oxo-bridging, and the solvent molecules complete the sixfold coordination of zirconium. In view of the fact that EXAFS spectroscopy provides information about the short range order only, we could not decide whether the obtained structure is part of a ring or chain-like oligomer.

Summarizing our results we conclude from the analysis of the EXAFS spectra of the sol and gel precursors of PZT that a uniform composition on a microscopic scale exist in both states. It facilitates the conversion of amorphous material to crystalline PZT, since essential structural subunits are already preformed and the short diffusion paths favour chemical reactions or structural changes.

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