

Preparation and Properties of Sol-Gel-Derived PZT Powders

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ABSTRACT

Lead-zirconate-titanate powders (PZT, $Pb(Zr_{0.54}Ti_{0.46})O_3$) were produced by the sol-gel route via (1) gelation of a sol, (2) precipitation from a sol, and (3) precipitation from an emulsion. The size of the colloidal particles in the sol, grain size of the powders and their specific surface areas were determined, and the development of the powder during pyrolysis and calcination was followed by infrared spectroscopy, differential thermal analysis and X-ray diffractometry. PZT was formed between 500 and 600°C regardless of the preparation technique and the difference in grain size and specific surface area.

INTRODUCTION

Lead-zirconate-titanate (PZT) is a piezoceramic compound which crystallizes in the perovskite structure. PZT is widely used as an actuator and sensor material. It displays its most favourable piezoelectric properties near the morphotropic phase boundary between the rhombohedral and tetragonal modifications at a composition of $Pb(Zr_{0.54}Ti_{0.46})O_3$. Dopants (Nd, La, etc.) may enhance the desired electrical properties and influence the sintering behaviour of the PZT powder [1].

The preparation of PZT powders by chemical methods has been performed by a large number of laboratories in recent years, *e.g.* [2-4]. There appear to exist some advantages inherent to this method which cannot be matched by other powder preparation techniques. These advantages are low calcining temperatures, low sintering temperatures, close control of chemical composition and good homogeneity of dopant distribution due to mixing of the components in the liquid state.

Especially the low calcining and sintering temperatures in combination with high density of the sintered material may offer a chance to develop piezoceramic devices with improved properties. However, utilizing and exploiting these potentials requires further knowledge about the reaction parameters and the influence of certain processing steps on the properties of the final product. Systematic efforts in this direction are sparse and optimum conditions for PZT powder preparation via the sol-gel process cannot be deduced unequivocally due to the variety of preparation techniques and analytical methods used by different laboratories.

It was the aim of our study to prepare PZT powders by different sol-gel methods and to compare their properties by the same analytical methods. In this paper we concentrate on the properties of the powders during the preparation, pyrolysis, and calcination procedure.

POWDER PREPARATION

Three different methods were chosen for powder preparation, in order to assess the influence of the preparation technique on the properties of the powders. Starting compounds were Pb-acetate, Zr-i-propoxide, and Ti-ethoxide for method 1 and 2, and Pb-nitrate for method 3. The first method produces a dried gel which has to be ground to achieve a proper grain size distribution before pressing and sintering. In the second method a powder is directly precipitated from a sol. Method 3 was developed in order to reduce the large amount of organic compounds from the sol prior to calcination.

Method 1: Pb-acetate was dissolved in methanol at 65°C. Separately, Zr-i-propoxide and Ti-ethoxide were blended in the respective quantities, and acetic acid was added. Acetic acid was found to prevent spontaneous hydrolysis and condensation of the alkoxides, probably by the formation of complexes. Other complexing agents (*e.g.* acetylacetone) were introduced as well and also strongly reduced the rate of hydrolysis and condensation. The Zr-Ti solution was added to the dissolved Pb-acetate under stirring, and water was added to start hydrolysis. A gel formed within a few minutes, but a low viscosity was regained after ageing overnight at room temperature. The evaporation of the solvents again initiated gelation, and a light brown mm-sized powder was obtained after drying at 110°C.

Method 2: A sol was prepared according to the method described above, and acetone was added. Fall-out of a white powder occurred instantaneously, but redissolved readily as long as the overall concentration of the acetone was low. Increasing the acetone concentration and washing and redispersing the powder several times lead to an extremely fine-grained (100 nm) white powder which was stable in air, water, and alcohol. Insufficient acetone washing led to the formation of a gel from the powder when exposed to air.

Method 3: Zr-i-propoxide and Ti-ethoxide were dissolved in ethanol. The Zr-Ti alkoxide solution was acid hydrolysed with diluted HNO₃ and excess water. The solvents were evaporated by distillation and the resulting substance was redissolved in water. This step was repeated until the alcohols used as solvent or formed during hydrolysis and condensation were extracted. This procedure yielded an acidic Zr-Ti-hydroxide sol. Pb-nitrate was dissolved in distilled water and added to the sol.

An emulsion was prepared from this stable solution in petroleum ether and an emulgator by vigorous stirring with a high-speed blender. Condensation of the droplets was initiated by the introduction of gaseous NH₃ to the emulsion, causing precipitation of a powder. The resulting powder was repeatedly washed in ethanol under NH₃ atmosphere, filtered and dried.

RESULTS

Characterization of the sol

The sol prepared by method 1 was characterized in terms of viscosity and particle size distribution. The kinematic viscosity was measured over a period of 190 hrs (Figure 1). Within the first 5 hrs the viscosity dropped markedly until it reached its final value (some 20% below the starting value).

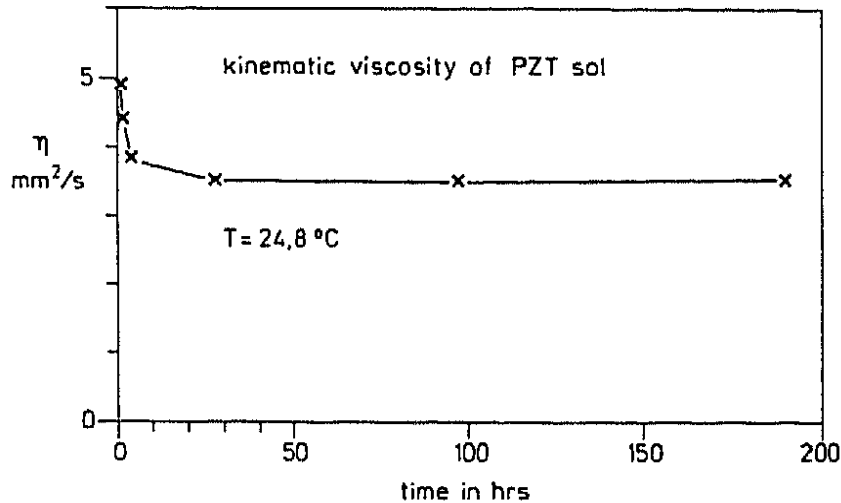


Figure 1. Kinetic viscosity of a PZT sol prepared by method 1.

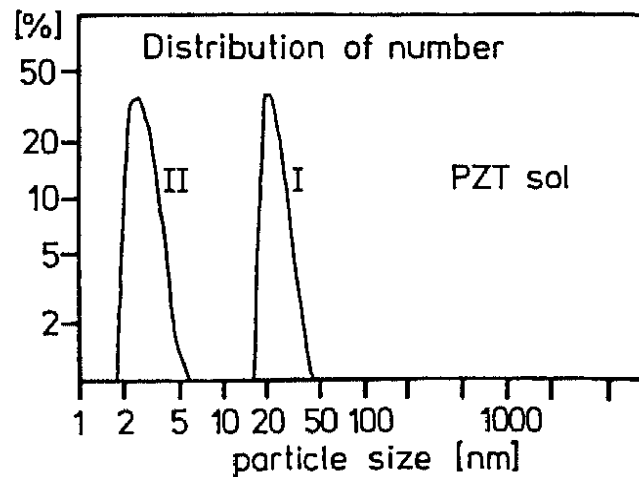


Figure 2. Size distribution of colloidal particles in a sol prepared by method 1; I: original sol, II: sol with acetylacetone as complexing agent.

The size distribution of colloidal particles in a sol aged for two weeks in a closed flask at RT was analysed by a dynamic light scattering technique. The maximum of the size distribution is between 20 and 30 nm, and the distribution is narrow and peaked (Figure 2). A minimum particle size of a few tens of nanometers may consequently be expected by the precipitation of a powder from this sol. Gelation should result in an increase in particle size, but unfortunately the particle size could not be measured in the early gel stage (shortly after preparation) and at a late stage after partial evaporation of the solvents because the transparency of these gels was too low. The introduction of a complexing agent (*e.g.* acetylacetone) during sol preparation resulted in the development of particles which are only 2–3 nm in size (Figure 2) even after ageing the sol for one year. The structure and chemical composition of these particles is not yet known, but evidently mixing of components in the sol-gel process occurs among particles which are at least a factor of 50 smaller than used by the mixed oxide method.

Powder characterization

Powders were prepared by milling the dried gel in a ball mill, by spray-drying and freeze-drying sols, and by precipitation from the sol or from the emulsion.

Grain size and specific surface area

According to the different preparation methods, the powders display different characteristics. The shape of the ball-milled gel powder particles is isometric, the average grain size after 5 min dry milling is 5–6 μm with 90% of the grains smaller than 10 μm . Spray-dried sols produced spherules some of which were hollow, which proved unfavourable for further processing. The average size of the spherules was 3–5 μm . In contrast, freeze-drying of the sol resulted in platelets, about 10 μm long and 1 μm thick. Precipitation from the sol yielded isometric particles 50–100 nm in dimension which agglomerated to μm -sized irregular bodies. Similar results were obtained from the emulsions, although the agglomeration rate is higher than with the precipitated powders.

The development of the size of individual crystals upon heating was followed by X-ray techniques. Grain size estimates of crystalline sub-grains after calcination of the powders at 800°C for 2 hours obtained from the broadening of X-ray diffraction lines still gave values well below 300 nm. After annealing for 2 hours at 1200°C the X-ray lines were sharp and narrow which indicates μm -sized crystals and improved crystallinity.

The specific surface area of the powders was determined by N_2 -adsorption at -196°C after drying the powdered substances for 16 hours at 110°C. Single point BET-measurements were performed (Table 1). The powders prepared by method 1 yielded specific surface areas of < 1 to 2.5 m^2/g . There is only a slight dependence of the surface area from the calcination temperature. Spray-dried powders and freeze-dried powders gave less than 3.3 m^2/g . In contrast, precipitated powders — as expected from their morphology and grain size — showed much higher values, 50 to 80 m^2/g for those precipitated with acetone

Table 1. Specific surface area of PZT gels and powders (N_2 -BET)

<i>Sample</i>	<i>Condition</i>	<i>Specific surface area [m^2/g]</i>
Method 1 (gel)	110°C	0.5
	150°C	1.0
	500°C	< 0.4
	600°C	2.5
	660°C	2.4
	800°C	< 0.5
Method 2 (sol)	spray dried	3.3
	freeze dried	1–2
	precipitated 110°C	50–80
Method 3 (emulsion)	emulsion	
	110°C	126
	600°C	3.4

and $126 \text{ m}^2/\text{g}$ for those prepared from the emulsion. The powder prepared by precipitation from the emulsion almost loses its specific surface area totally when heated to 600°C .

IR absorption spectra

The development of PZT powders from a dried gel to the crystalline powder is revealed by infrared absorption spectra (Figure 3) taken at room temperature from samples heated before to 100 to 650°C (KBr pellets). After heating to 100°C , the absorption bands of vibrations typical of alcohol, water, and acetate may be distinguished. In addition there is a vibration indicative of CO_2 which most probably is due to adsorbed CO_2 . Heating to 300°C changes the spectra drastically, water and alcohol are no longer detectable and the vibrations interpreted as being due to acetate are very weak. At 500°C these vibrations vanish as well, and weak bands typical of perovskite develop. These absorption bands and shoulders are indicated by arrows in the spectrum taken from samples heated to 650°C .

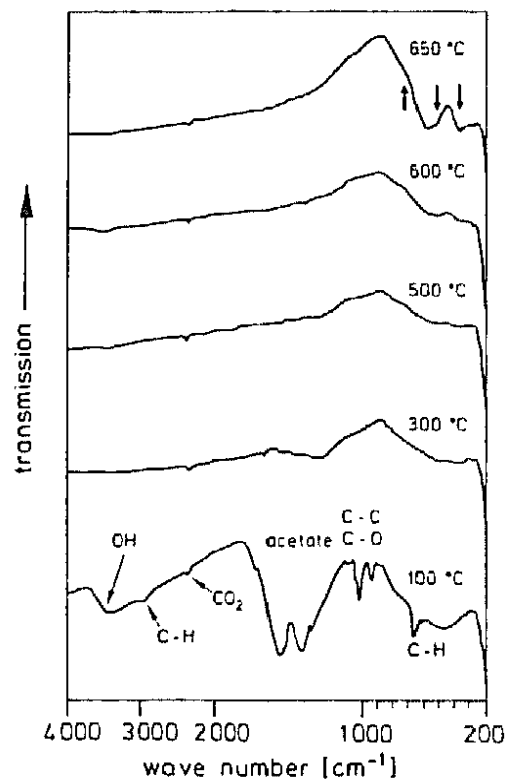


Figure 3. Infrared absorption spectra of powders prepared according to method 1. Arrows: absorption bands and shoulders of perovskite.

There are no major differences between the IR spectra of samples prepared by methods 1 and 2. The infrared spectra indicate the formation of PZT at temperatures of about 500°C which is considerably lower than the temperature required for PZT formation by the mixed oxide technique.

Differential thermal analysis

Differential thermal analysis (DTA) of a gel powder prepared by method 1 combined with thermogravimetric analysis (TG) and a quadrupole mass

spectrometer (MS) (Figure 4) displays strong exothermic and endothermic reactions most of which may be correlated with weight loss. A broad endothermic peak at 100°C with minor weight loss is due to evaporation of water probably reabsorbed to the gel powder which had been dried at 100°C before the analysis. At 250°C a strong endothermic feature is correlated with loss of water and CO_2 as determined by mass spectroscopy. Small amounts of organic material have also been detected. This endothermic reaction was interpreted as melting of Pb-acetate by [5]. At 500°C another loss of CO_2 corresponds with an exothermic peak and is correlated with the oxidation of organic compounds. A small exothermic feature at 600°C without a change in sample weight is interpreted as heat of crystallization of PZT, but crystallization might also be responsible for the exothermic reaction at 500°C which, however, coincides with the simultaneous disintegration of organic compounds.

At temperatures above 650°C no change in enthalpy nor weight change is observed. The total weight loss during heating from 100°C to 650°C is 25%. The respective DTA, DTG and MS curves of sample 2 again are very similar to

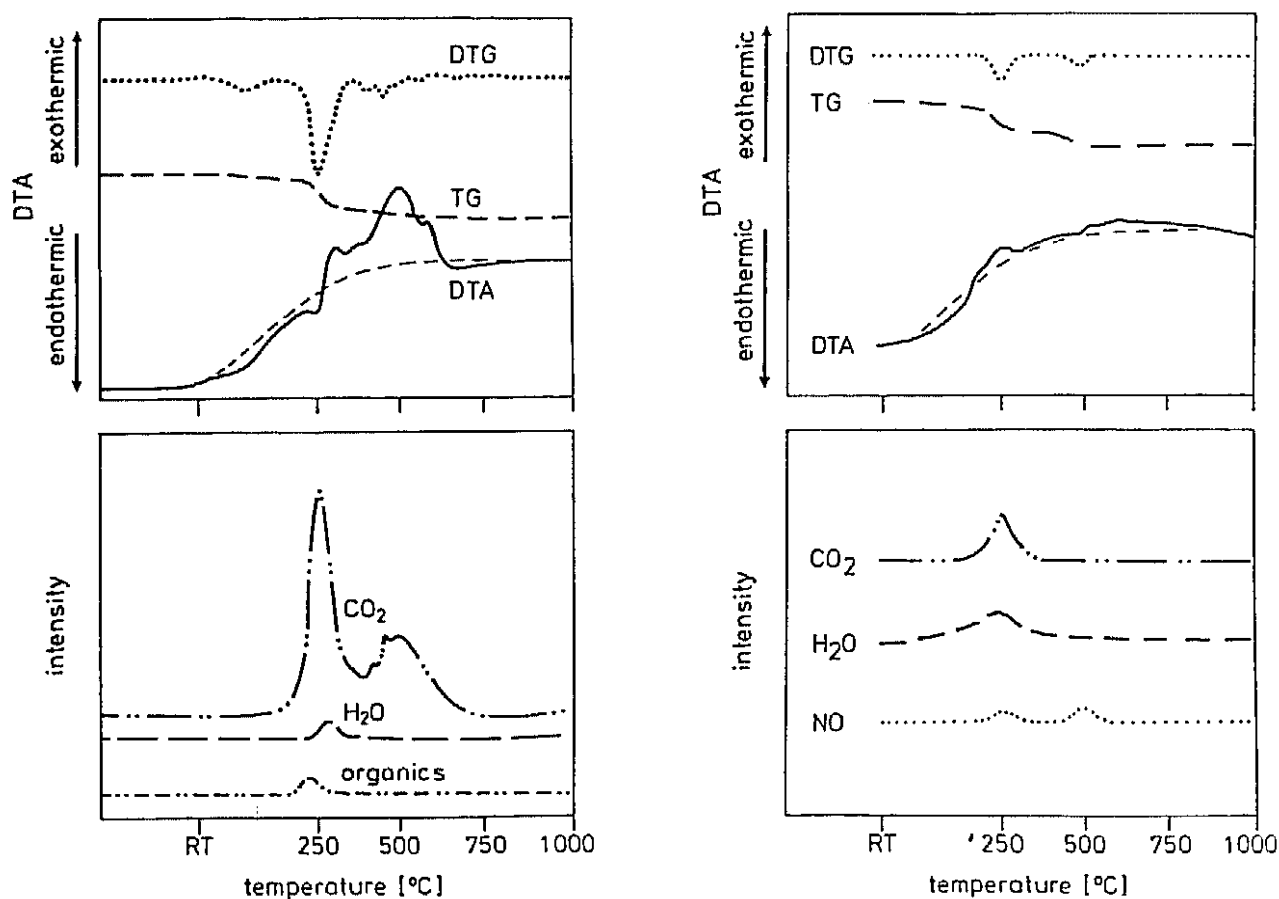


Figure 4. DTA/DTG and mass spectra of PZT powders 1 (left) and 3 (right).

those of sample 1. Powders prepared from the emulsion (method 3) show a different behaviour. Due to the reduction of the amount of organic solvents by repeated washing, the total weight loss of the sample between 100 and 600°C is only 10% compared with 25–30% of the powders 1 and 2 (Figure 4).

The first weight loss is correlated with an endothermic peak at $250\text{--}260^{\circ}\text{C}$,

where water, CO_2 , and NO are recorded in the mass spectrum. A second endothermic feature shortly below 500°C and again correlated with a weight loss is due to the disintegration of unreacted Pb-nitrate. Crystallization of PZT is less pronounced and may be responsible for the small exothermic features apparent above 500°C .

X-ray powder diffraction

Crystallization of PZT from the dried gel was monitored by X-ray diffraction spectra (Figure 5). The powder patterns were taken at room temperature. Heating time was 2 hours under atmospheric conditions. Heating to 100°C produced a more or less X-ray amorphous substance with weak indications of the strongest PZT peak at $30^\circ 2\theta$. In concordance with the infrared spectra, at temperatures above 500°C crystalline PZT developed. At 600°C only PZT and small amounts of PbO have been detected. PbO combines with the remainder to form PZT at 660°C . This combination may be achieved also at 600°C by heating for more than 10 hours. At temperatures of 650°C PbO loss by volatilization is unlikely and no weight loss was detected at this temperature by thermogravimetric analysis. Therefore, compound formation is the most likely alternative. This view is supported by the chemical analysis of powders heated to 800°C which also did not reveal PbO loss.

While the X-ray data of samples prepared by methods 1 and 2 were almost identical, the powder prepared from the emulsion did not reveal diffraction

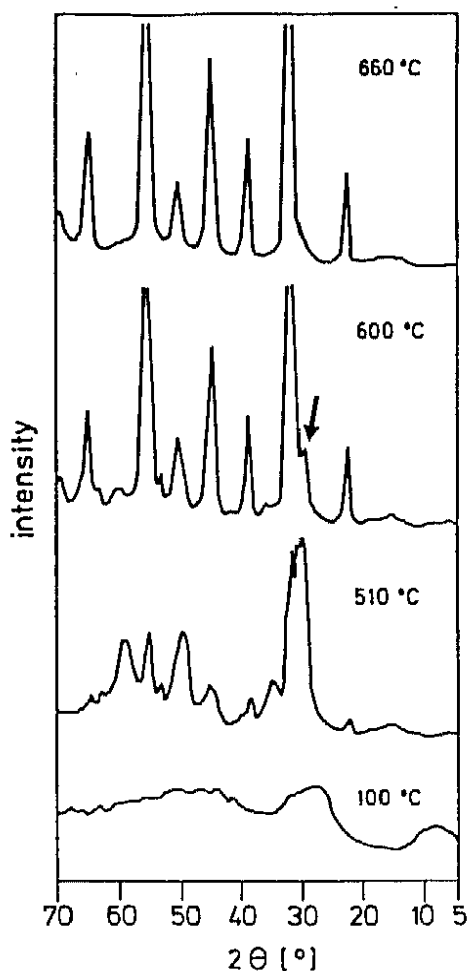


Figure 5. X-ray diffractograms of powder 1. Arrow: PbO, formed as an intermediate phase.

peaks indicative of PbO after 2 hrs at 600°C. Only PZT peaks were observed. PbO either develops by melting of Pb-acetate [5] or by the reduction of Pb-compounds to Pb during the pyrolysis of organic ligands at temperatures between 250 and 500°C. Pb once molten may even tend to aggregate to droplets on the surface of PZT grains forming PbO crystals upon further oxidation. Pure PbO crystals were observed by SEM in some samples.

Scanning transmission electron microscopy

In order to determine the grain size and chemical homogeneity, STEM analyses were performed on calcined powders (2 hours, 800°C) precipitated from the sol. Chemical analysis was done with an energy dispersive X-ray detector (EDX) with a spot size of 7.5 nm to reach higher resolution.

Figure 6 shows an agglomerate consisting of particles, most of which are 100 nm in size. The EDX mapping for Zr displays a homogeneous distribution of this element throughout the sample. Identical results have been obtained for Pb and Ti. These photographs clearly depict the advantage of the sol-gel method for the production of chemically homogeneous precursor powders at low temperatures.

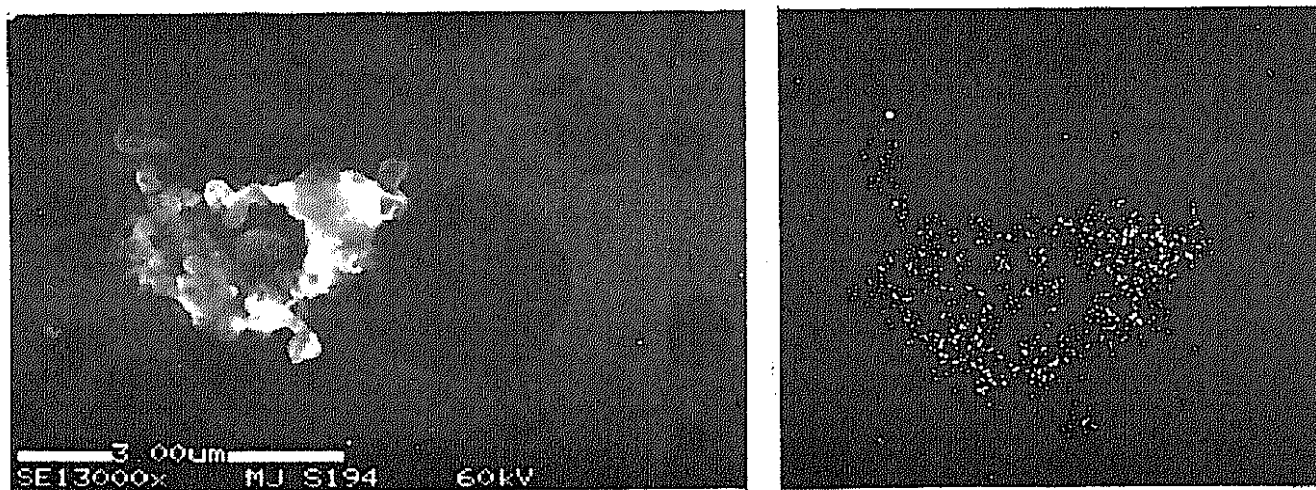


Figure 6. Left: SEM picture of an agglomerate (powder 2). Note the small size of the individual particles (about 100 nm). Right: Elemental mapping (Zr). Scanning transmission electron microscope (STEM), spot size 7.5 nm, scale bar: 3 μm.

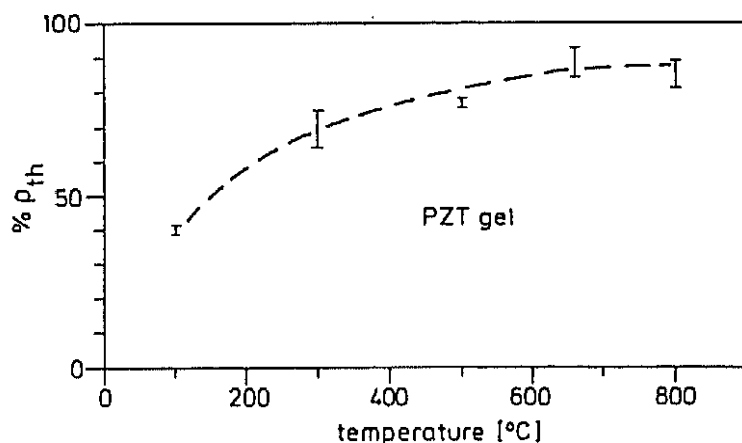


Figure 7. Densification of PZT gel during pyrolysis and calcination (method 1).

Density of gel powder

The extreme shrinkage of sol-gel derived powders has been noted before. Pressureless sintering of mm-sized gel pieces should reveal the increase in density and the degree of densification of monolithic gels as a function of temperature. The density increases markedly with the loss of organic substances between 100 and 500°C, then levelling off at values between 85 and 90% of the theoretical density at 800°C (Figure 7). Monolithic gels thus retain a porosity of more than 10%, and to achieve dense ceramic bodies grinding and pressing prior to sintering appears necessary.

Sintering

A pellet of a powder prepared by method 1 and calcined at 800°C was prepared by isostatic pressing and subsequent sintering at 1180°C for 2 hrs together with excess PbO. A fracture surface of this pellet is shown in Figure 8. During sintering, crystalline particles of 0.5 to 2 µm developed from the gel powder, which had an average grain size of 5 µm. Elemental mapping by EDX revealed no inhomogeneities within and among the individual PZT grains.

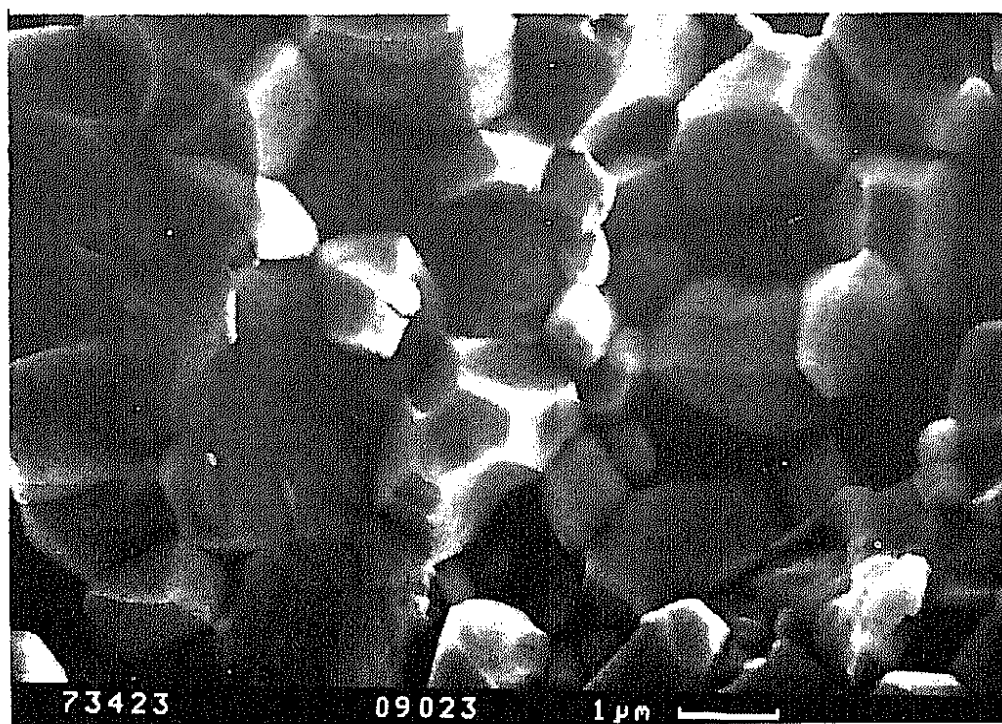


Figure 8. Fracture surface of powdered gel (method 1), calcined at 800°C, sintered at 1180°C. SEM picture, scale bar: 1 µm.

CONCLUSIONS

The properties of PZT powders prepared by the sol-gel method are highly susceptible to the preparation methods employed. The introduction of a complexing agent during the sol preparation reduces the size of the colloidal particles from 20–30 to 2–3 nm. Precipitation of powders from an emulsion or from a sol results in a 10- to 100-fold increase in specific surface area when compared with a powder prepared from a PZT gel. All powders develop PZT

at temperatures above 500°C. PZT formation is complete at 600°C, but PbO was observed in small amounts at this temperature as well. At 650°C only PZT was detected. Pure PZT was obtained at 600°C when the organic solvents were removed from a hydrolysed sol by multiple washing with water. All PZT powders are chemically homogeneous and highly reactive.

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