

# SOLUTION SYNTHESIS OF Pb(Zr,Ti)O<sub>3</sub> CERAMIC NANO-POWDERS

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**Key words:** Pb(Zr,Ti)O<sub>3</sub> (PZT), nano-powder, solution synthesis, ceramics

**Abstract:** Solution synthesis of multicomponent ceramic materials, such as Pb(Zr,Ti)O<sub>3</sub> (PZT), should yield better homogeneity, chemical purity and lower processing temperatures as a consequence of nano-meter range particle size in comparison to solid state synthesis.

Synthesis of stoichiometric PZT ceramic powders with the Zr/Ti ratio 50/50 based on hydrolysis of n-butoxide-derived heterometallic complex was found to yield loosely agglomerated powders consisting of about 100 nm-sized aggregates that could be sintered to almost theoretical density at 1000°C, a temperature a few 100 °C lower than those typically used for solid-state synthesized ceramics.

## Priprava nano-prahov Pb(Zr,Ti)O<sub>3</sub> (PZT) iz raztopin

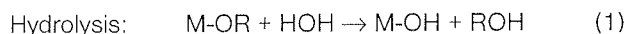
**Ključne besede:** Pb(Zr,Ti)O<sub>3</sub> (PZT), nano-prah, sinteza iz raztopine, keramika

**Izvleček:** Sinteza iz raztopin večkomponentnih keramičnih materialov, kot na primer Pb(Zr,Ti)O<sub>3</sub> (PZT), omogoča doseganje večje homogenosti, čistoče in nižje procesne temperature v primerjavi s klasično sintezo v trdnem stanju.

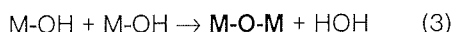
Sinteza prahu Pb(Zr,Ti)O<sub>3</sub> z razmerjem Zr/Ti 50/50, ki ga sestavljajo približno 100 nm agregati, temelji na hidrolizi heterometalnega butoksidnega kompleksa. Keramiko s skoraj teoretično gostoto pripravimo po toplotni obdelavi pri 1000 °C, kar je nekaj 100 °C nižje od značilnih temperatur sintranja keramike, pripravljene s sintezo v trdnem stanju.

### Introduction

In the last years the research of the solution synthesis of ceramic powders has increased due to the potential advantages of better homogeneity, chemical purity and nanometer-range particle size in comparison to the solid state synthesis. Alkoxide based sol-gel processing is one of the various solution syntheses; it is based on the reactions of hydrolysis and polycondensation of metal alkoxides M(OR)<sub>n</sub> shown schematically by Eq. 1 – 3 [1,2]. In the first reaction the reactive alkoxide groups are exchanged by hydroxyl groups in the extent depending on the amount of water and in the following ones the metal-oxygen-metal bonds are formed.



Polycondensation:



Schematic representation of the reactions of one alkoxide group.

M: metal atom, -OR: alkoxide group, -R: alkyl group

Transition metal (TM) alkoxides, i.e. Ti- or Zr- alkoxides, are extremely sensitive to the nucleophilic attack of water due to their low electronegativity and a possibility to increase their coordination number. The products are typically oligomeric units where the type and amount of functional groups – hydroxyl, alkoxide, oxo – depend on the reaction conditions, type of the alkoxide group and amount of water used for hydrolysis [1].

In the case of multicomponent systems, typically those for functional ceramics, the first step of the process is the synthesis of a heterometallic alkoxide or a complex based on simple alkoxides and metal salts. In the next step, this intermediate product is hydrolysed to yield a precursor powder, usually amorphous, whose morphology depends on the choice of the reactants and the reaction conditions. In the further heat-treatment steps, i.e. drying, pyrolysis and crystallisation, a crystalline powder with the stoichiometry of the target material is obtained, typically at lower temperatures than those required in the solid state synthesis [3].

The properties of the units of a ceramic powder – crystallites, aggregates and agglomerates essentially determine the cold compaction behaviour of the powder, therefore

the pore size distribution in the green compact, sintering and the microstructure of the ceramics /4/. The use of non agglomerated, chemically pure, nano-powders with a narrow particle size distribution can lead to dense ceramics with a fine-grained microstructure and a narrow distribution of pores /5/. The fine particle size allows reaching high density at lower sintering temperatures that are typical for classically prepared ceramics. The lowering of the sintering temperature is important for the ceramics, containing components with a high vapour pressure such as  $\text{PbO}$ , as for example  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  solid solution /6/.

The comparison of the processing steps of PZT ceramics by solid-state and solution synthesis is shown in Figure 1.

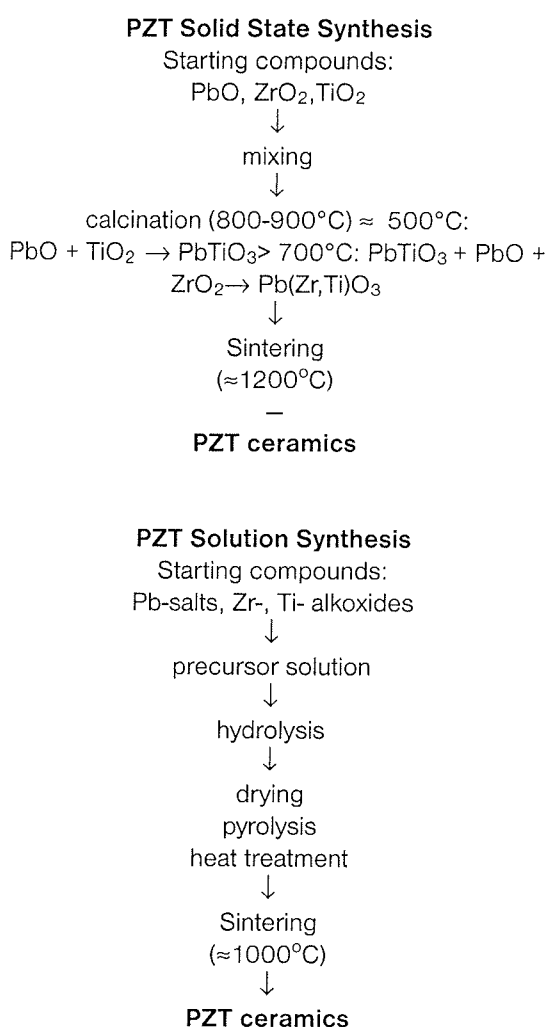


Figure 1: Comparison of the solid-state and solution processing of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  ceramics.

The present contribution summarises an overview of the authors' work in the field of novel ceramic processing of PZT based ceramics /7-11/ with the emphasis on the correlation between the solution chemistry – the choice of the starting compounds and reaction conditions that determine the structure and reactivity of the heterometallic precursor and the physical properties of the ceramic pow-

der – the particle size, agglomeration state and its sinterability.

## EXPERIMENTAL

The manipulation of chemicals was carried out in dry nitrogen atmosphere due to great reactivity of alkoxides towards humidity. The reactions were performed by standard Schlenk technique. The flow sheet is shown in Fig. 2.

Dehydrated lead (II) acetate ( $\text{Pb}(\text{OAc})_2$ , JM Alfa, ultra pur) and TM n-propoxides and n-butoxides ( $\text{TM} = \text{Zr}, \text{Ti}$ ,  $\text{TM}(\text{On-Pr})_4$ ,  $\text{TM}(\text{On-Bu})_4$ , JM Alfa, metal content determined gravimetrically) were used for the synthesis of heterometallic  $\text{Pb}(\text{Zr,Ti})$ -precursors with  $\text{Zr/Ti} = 50/50$ . Pb-Ti and Pb-Zr precursors were also prepared. The solvent was the parent alcohol, n-propanol or n-butanol, respectively. Typically, the batch was between 25 and 75 millimoles. The reactants were dissolved upon heating, refluxed, distilled to remove the by-products. The 0.25 M solution was hydrolysed with 10 moles of deionised water/mole of Pb-acetate to yield a suspension. After drying at  $60^\circ\text{C}$  and  $150^\circ\text{C}$  the amorphous precursor powder was heated at  $650^\circ\text{C}$  for 5h in flowing oxygen. The ceramic powders were milled for 120 min. in parent alcohol and dried at  $100^\circ\text{C}$ . The green compacts were prepared by uniaxially pressing at 50 MPa and isostatically at 500 MPa. The pellets were sintered at a heating rate of  $10^\circ\text{C/min.}$  with  $\text{PbZrO}_3$  as packing powder.

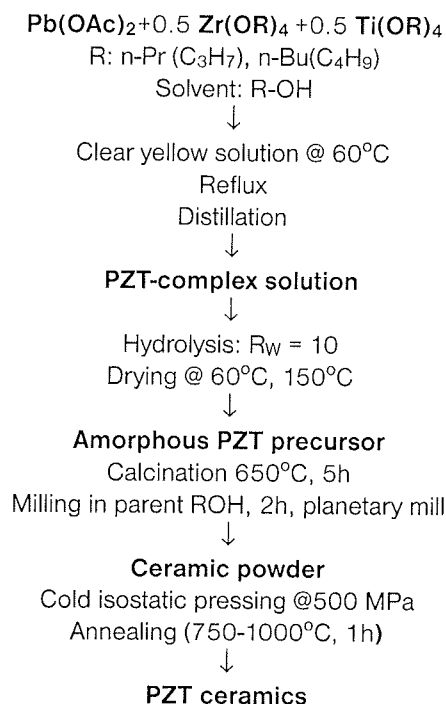


Figure 2: PZT precursor synthesis and processing.

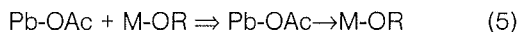
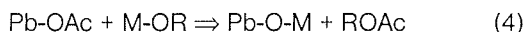
The volatile reaction by-products were analysed by gas chromatography (GLC, FFAP 5% on Chromosorb W, TC, He) with methylphenylether as an internal standard.

The morphology of the powders was analysed by SEM (Leitz AMR 1600T, JEOL JXA 840A). Particle size distribution was determined by laser granulometry (Cilas Alcatel) and the specific surface by BET (Perkin Elmer 212D). Thermogravimetry was performed in air at a heating rate of 10 °C/min (Netzsch, STA 429). The density of ceramic samples was determined picnometrically. The samples for microstructural analysis were prepared by thermal etching (60 sec at the sintering temperature). The average equivalent grain diameter was calculated from the grain areas by measuring approximately 200 grains.

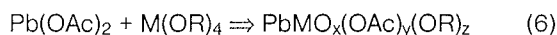
## RESULTS AND DISCUSSION

### Synthesis of the heterometallic precursors

The synthesis of the heterometallic complex occurs by a reaction between Pb-acetate and TM-alkoxides upon dissolution in the parent alcohol. This reaction can proceed either by ester elimination (Eq. 4) and/or addition (Eq. 5) /3,12-14/. (The reactions below are schematical, for one functional group per reactant.) The former reaction leads to the formation of oxo (-O-) bridges and the latter to the formation of acetate bridges between Pb and TM atoms.



In reality both reactions occur, leading to a product containing oxo, alkoxo and acetate groups (Eq. 6).



The presence of alkylacetates in the distillates, that is in the by-products of the reaction between Pb-acetate and TM-alkoxides, was determined by GLC analysis. Distillation residue could not be analysed due to extreme sensitivity to humidity. The alkylacetate/alcohol (ROAc/ROH) ratios for propoxide and butoxide derived Pb-Zr and Pb-Ti complexes are shown in Fig. 3. For both Pb-Zr and Pb-Ti the (ROAc/ROH) ratio is noticeably higher for the butoxide-derived complexes. We therefore conclude that the ester-elimination reaction (Eq. 4) contributes more in the butoxide system than in the propoxide one, hence the butoxide-based reaction product contains fewer alkoxide and acetate groups than the propoxide based one.

The hydrolysed Pb-TM complex is schematically described as [PbMO<sub>x1</sub>(OAc)<sub>y</sub>(OR)<sub>z1</sub>(OH)<sub>w</sub>]<sub>n</sub>. The alkoxide groups are partially removed by hydrolysis while the acetate ligands remain bonded to metal atoms. The presence of hydroxyl and acetate groups in both propoxide- and butoxide-derived as-dried precursors has been qualitatively confirmed by FTIR /11/. Thermal decomposition of as-dried Pb-Zr-Ti precursors was followed by thermogravimetry in order to determine the relative amounts of hydroxyl and organic groups (Figure 4).

The propoxide based precursor decomposes upon heating to 550 °C in three steps, with the total weight loss of

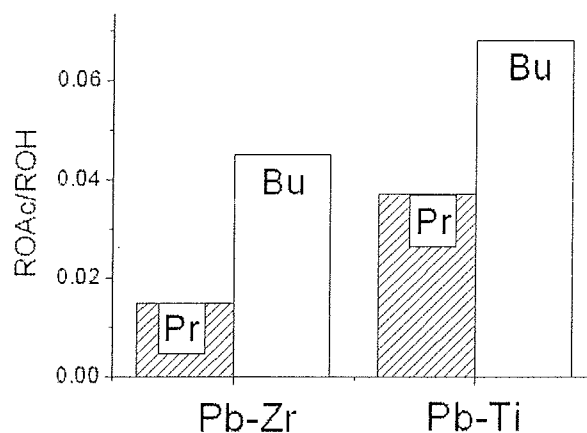


Figure 3: Alkylacetate (ROAc)-alcohol (ROH) ratio in distillates formed in the reaction between Pb-acetate and Zr- or Ti-alkoxide (R= Pr,Bu), respectively determined by GLC. Note that the azeotropic mixtures for PrOH/PrOAc and BuOH/BuOAc are similar /15/ therefore a comparison of the two systems is reasonable. (From /11/).

about 13 %, while the decomposition of butoxide-based precursor occurs in two steps upon heating to 400 °C, the total weight loss is 9 %. Additional characterization of the decomposing species by EGA (spectra not shown here, /7/) revealed that in both cases the first weight loss from room temperature up to 200 - 250 °C is due to water evolution, while at higher temperatures organic groups, i.e. acetate and alkoxide, are pyrolyzed. The relative amount of organic groups is higher in the propoxide-derived precursor than in the butoxide-derived one. This result is in agreement with the GLC results shown in Figure 3 namely that the amount of acetate groups in the propoxide-based complex is higher than the amount in the butoxide-based one.

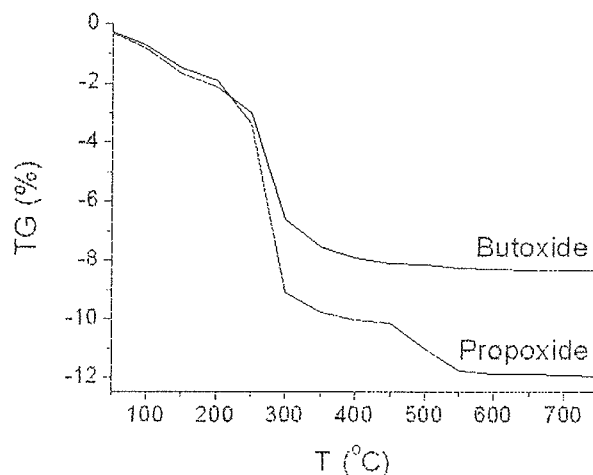


Figure 4: Thermal decompositions of propoxide and butoxide derived as-dried PZT precursors.

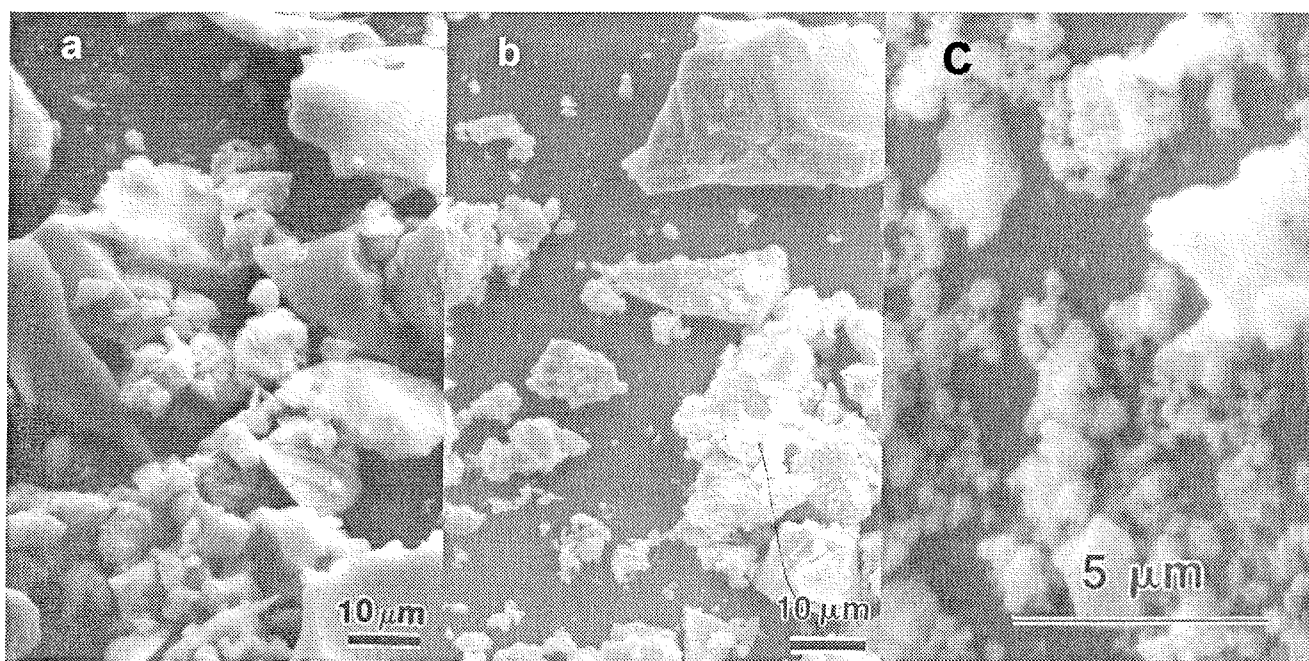


Figure 5: SEM micrographs of propoxide derived powder after drying at 150 °C (a), after heat treatment at 650 °C, 5h (b) and additional milling (c).

### Morphology of the dried and calcined PZT powders

Upon hydrolysis with an excess of water the propoxide complex forms a viscous opaque suspension, while the butoxide complex precipitates. There is a significant difference in morphology of the two powders (Figures 5, 6). The as-dried propoxide powder consists of irregularly shaped gel fragments with sizes up to 60 μm without a

noticeable texture. The morphology of irregularly shaped fragments ranging from a few to 60 μm is retained also after heating at 650 °C - the temperature required to remove organic residues and obtain pure perovskite phase /7/. By additional milling we achieve a partial desintegration of the gel fragments. The median particle size is reduced to 1 μm, nevertheless the irregular morphology of the powder is retained as it is clearly shown in the micrograph.

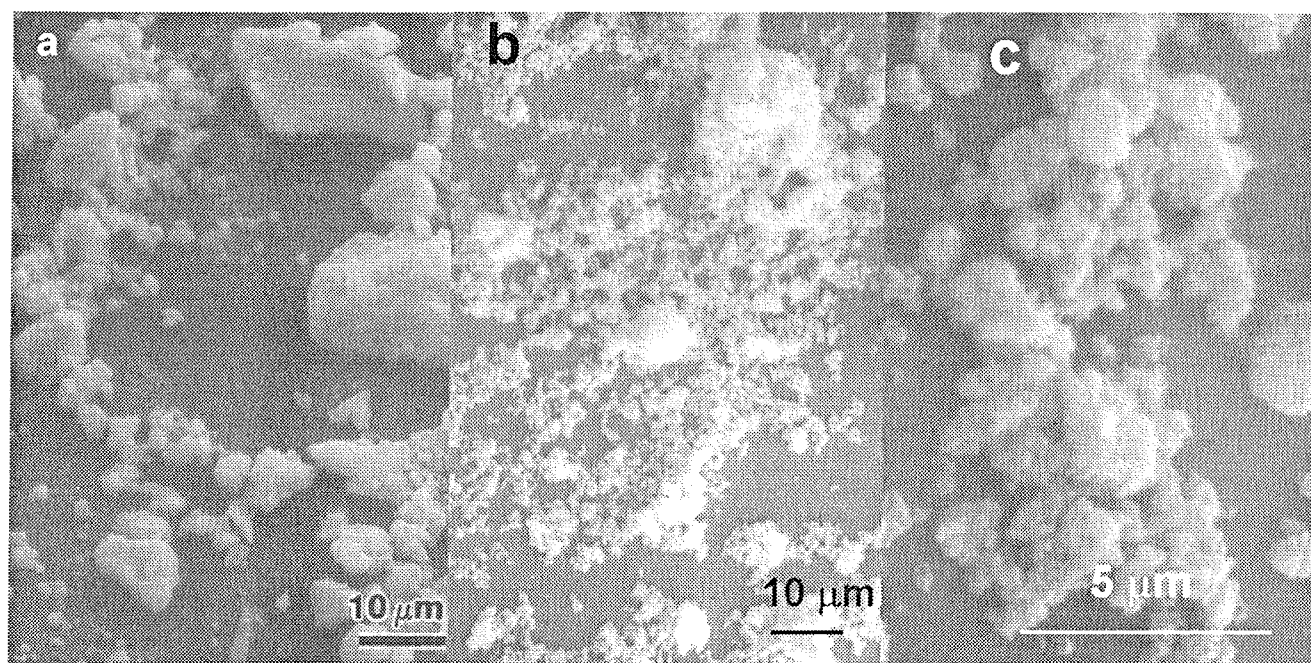


Figure 6: SEM micrographs of butoxide derived powder after drying at 150 °C (a), after heat treatment at 650 °C, 5h (b) and additional milling (c).

In contrast the butoxide derived powder is much finer after drying than the propoxide-derived one. It is composed of agglomerated submicrometer particles ranging up to  $60\ \mu\text{m}$  with the median value at  $10\ \mu\text{m}$ , with a clearly discernible texture. The BET surface area of  $192\ \text{m}^2/\text{g}$  equals the particle size of  $8\ \text{nm}$ . (Note that the BET measurement of the propoxide powder could not be performed – the powder decomposed during the measurement.)

After heating at  $650\ ^\circ\text{C}$  for 5 h the crystallite size determined from the broadening of XRD-peaks of the perovskite phase is  $30\ \text{nm}$  and the aggregate size calculated from the BET surface area is  $110\ \text{nm}$ . The median agglomerate size determined by laser granulometry is  $2\ \mu\text{m}$  with agglomerates ranging up to  $20\ \mu\text{m}$ . Presumably the agglomerates in the as-dried powder decompose upon calcining with coincident decomposition of the functional groups resulting in a similar effect as produced by milling. After additional milling of the butoxide powder the median agglomerate size is  $0.7\ \mu\text{m}$  with the largest agglomerates below  $2\ \mu\text{m}$  as determined by granulometry.

The comparison of the particle sizes of the propoxide and butoxide derived powders after calcinations and milling reveals only slightly higher values for the propoxide derived powder. Nevertheless the morphology of the two powders is significantly different: while the former consists of irregular fragments, the latter is composed of almost spherical units. In order to obtain further information about the strength of the agglomerates the compaction behaviour of propoxide and butoxide powders was compared (results reported elsewhere /9/). The gel fragments present in the as-calcined and milled propoxide derived PZT powder behave as hard agglomerates such as present in ceramic powders washed with water /16,17/. The powder compacts exhibit a broad pore size distribution. Quite the opposite the as-calcined and milled butoxide derived PZT powder results in a compact with a narrow pore size distribution such as it is typical for compacts of soft agglomerates composed of loosely bonded particles, that can be disintegrated by a low compaction pressure /4,17-19/.

### Sinterability of ceramic powders

The sintering curves of the two powder compacts were recorded by a heating-stage microscope (Figure 7), the results are expressed as density calculated from the mass and dimensions of the pellets vs. temperature. The onset of the shrinkage is at approximately  $900\ ^\circ\text{C}$  for both compacts. The propoxide-derived powder compact densifies over a broad temperature range, reaching the final value of 92 % at about  $1200\ ^\circ\text{C}$ . Quite the opposite the butoxide-derived compact shrinks in a narrow temperature interval, reaching the final value of about 96 % of theoretical density below  $1000\ ^\circ\text{C}$ . Such results have been indeed expected. The butoxide-derived compact is characterized by a fine particle size and a uniform and a narrow particle and pore size distribution therefore sintering to a high relative density occurs at a lower temperature as in the case of a larger particle size /20,21/. The presence of hard

agglomerates in the propoxide-derived powder hinders reaching high green density and high final density even if the particle size is small /5/.

The propoxide-derived powder compact was then sintered at  $1000\ ^\circ\text{C}$  for 2 h. The ceramic sample has got 96 % relative density and it is characterized by large lens-shaped defects in the microstructure (Figure 8). The result is in agreement with the observation that voids in the microstructure, typically a consequence of a nonuniform porosity distribution in the green compact, are the reason for reaching lower final densities /22/.

The butoxide-derived powder compacts were sintered between  $850\ ^\circ\text{C}$  and  $1000\ ^\circ\text{C}$  for 1 hour. The density and grain size data are gathered in Table 1. Density above 98 %TD is obtained at/above  $900\ ^\circ\text{C}$ . The grain size of PZT ceramics is in the micrometer range as evident from the microstructure of PZT sintered at  $1000\ ^\circ\text{C}$  for 1 h (Figure 9).

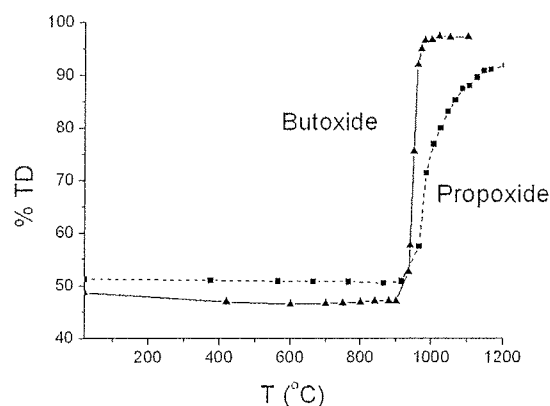


Figure 7: Dynamic sintering curves expressed as % of theoretical density TD vs. temperature of propoxide- and butoxide-derived PZT powder compacts recorded in air. Heating rate:  $5\ ^\circ\text{C}/\text{min}$ .  $\text{TD}_{\text{PZT}} = 8.00\ \text{g}/\text{cm}^3$ . (From /8/.)

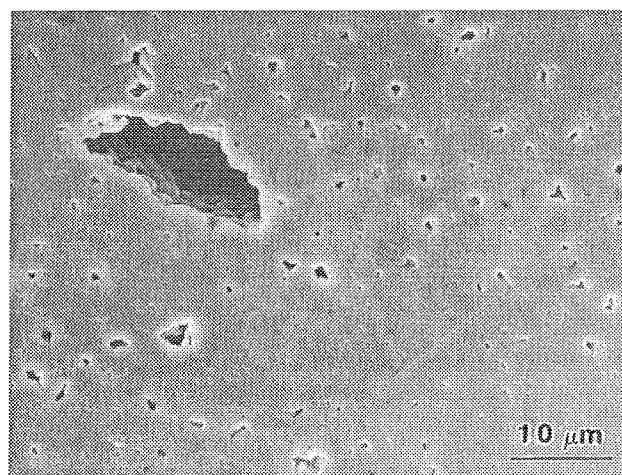


Figure 8: Microstructure of propoxide derived PZT ceramics, sintered at  $1000\ ^\circ\text{C}$  for 2 h. Relative density is 96 %. (From /9/.)



Table 1: Density (%TD) and grain size (d) of butoxide-derived PZT ceramics after heating at 850 °C and 1000 °C for 1 hour. (From /9/.)

T (°C)	% TD	d (μm)
850	89.0	0.9
900	98.6	1.0
950	99.8	1.2
1000	99.1	1.3

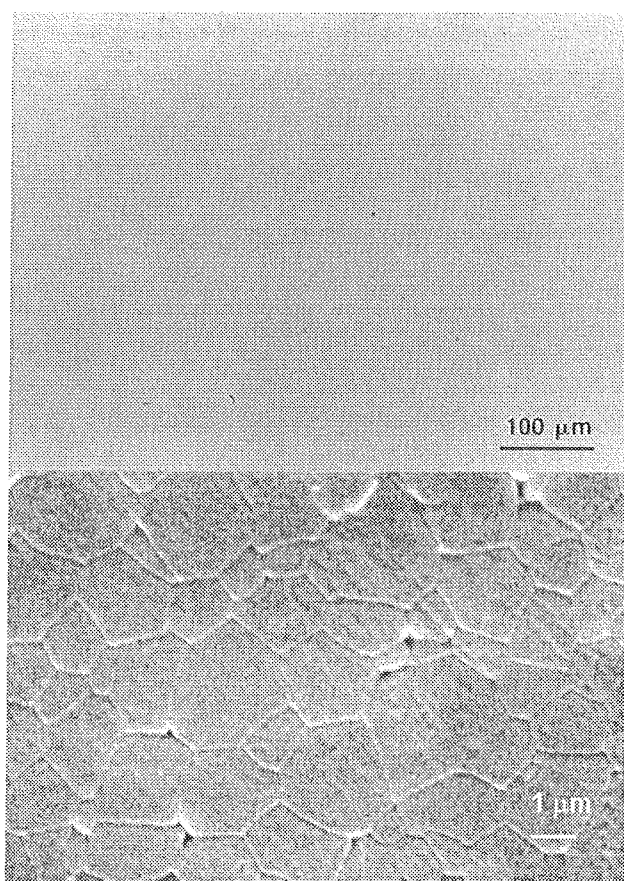


Figure 9: Microstructure of butoxide-derived PZT ceramics after heating at 1000 °C for 1 hour.

## Summary

Stoichiometric PZT 50/50 ceramics were prepared by alkoxide based solution processing. The choice of the starting alkoxides influences the reactions in solution and further particle formation upon hydrolysis of the heterometallic complex.

The hydrolysis of the propoxide-derived heterometallic complex yields a viscous opaque suspension, and upon

drying irregularly shaped gel fragments. This initial morphology is preserved upon further thermal treatment. As expected such powder results in ceramics characterized by large defects in the microstructure.

Butoxide-derived precursor yields a fine ceramic powder with a narrow particle size distribution. Sintering results in almost completely dense ceramics between 900 °C and 1000 °C with micrometer-sized grains.

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