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# $Pb(Zr,Ti)O_3$ based ceramics prepared by solution processing

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**Abstract**

Niobium and iron doped stoichiometric PZT ceramics (Zr/Ti 53/47, 2 at.% of dopant) were prepared by alkoxide-based solution processing. Sintering of both doped materials is severely inhibited in comparison to undoped PZT. TEM analysis of the ceramics, sintered at 1100 °C, revealed only a perovskite phase in the case of niobium doped PZT while the iron doped material contains entrapped zirconia particles and lead-enriched inclusions in the PZT matrix.

*Keywords:* Electron microscopy; Precursors-organic; PZT; Sintering; Alkoxides; $Pb(Zr,Ti)O_3$

## 1. Introduction

Solution processing of multicomponent materials, such as $Pb(Zr,Ti)O_3$ (PZT), should yield better homogeneity, chemical purity and lower processing temperatures as a consequence of sub-micron 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*-butoxides in *n*-butanol solution was found to yield loosely agglomerated submicrometer sized powders that could be sintered to almost theoretical density at 900 °C.[1] Incorporation of dopants by solution processing should in theory enable more homogeneous distribution of these ions in the concentration range of a few mol%. The aim of the present contribution was to study the phase composition and microstructural features of undoped, acceptor (Fe) and donor (Nb) doped PZT ceramic materials prepared in solution.

## 2. Experimental

Lead zirconate titanate solid solution [$Pb(Zr_{0.53}Ti_{0.47})O_3$, PZT] based ceramic materials were prepared by solution processing. Niobium or iron (2 at.%) were introduced into the solid solution by taking into account the fact that they occupy B-sites in the perovskite lattice, niobium acting as a donor, causing A-site vacancies and iron as an acceptor, causing vacancies in the oxygen sublattice.[2] The materials are further denoted as PZT, PZT–Nb and PZT–Fe, respectively.

The synthesis of the heterometallic complex solutions was performed in a dry argon atmosphere. Anhydrous Pb (II) acetate was dissolved in a solution of Zr and Ti *n*-butoxides in *n*-butanol. The dopants were introduced as niobium ethoxide or iron 2,4-pentanedionate. All chemicals were reagent grade (Alfa), and the metal content of the alkoxides was determined gravimetrically. The concentration of the metal compounds in alcohol was approximately 0.2 molar. After refluxing and distillation of the by-products, i.e. alkylacetate in alcohol, the solution was hydrolyzed with 10 moles of water per mole of Pb acetate. The resulting suspensions were dried at 150 °C and calcined at 600 °C for 5 h. Milling of the powders was conducted in a planetary mill in *n*-butanol for 120 min. The compacts were isostatically pressed at 500 MPa. Ceramic samples were annealed at temperatures up to 1200 °C.

Thermal analysis (thermogravimetry TG and differential thermal analysis DTA, Netzsch STA 409) was performed in platinum crucibles, in an atmosphere of flowing air at a heating rate of 10 °C/min. Sintering curves were recorded by a heating stage microscope (Leitz) at a heating rate of 10 °C/min. The phase composition was determined by XRD (Cu $K_\alpha$ radiation, Philips PW 1710). Microstructural analysis was performed by a scanning electron microscope (Jeol 5800) and analytical electron microscope operating at 200 kV (Jeol2000 FX EM) with a Link AN-10000 EDXS system.

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## 3. Results

Thermal decompositions of the as-dried amorphous powders studied by TG/DTA reveal quite similar pathways, with total weight losses of 12.8, 12.5 and 13.3%, the majority of the weight loss taking place between 250 and 350 °C accompanied by a single major exothermic effect (release of organics) at 285, 289 and 298 °C for PZT, PZT–Nb and PZT–Fe, respectively. Crystallization of the perovskite phase as confirmed by XRD is marked by an exothermic peak at 498 °C for PZT and at 515 °C for both doped PZT-precursors. TG/DTA curve of PZT precursor powder is shown in Fig. 1.

The powders calcined at 600 °C crystallize into pseudo-cubic perovskite structure. After milling they are composed of 1-μm sized agglomerates of 100–200 nm sized particles as observed by SEM.

Fig. 2 shows densification curves of the PZT, PZT–Nb, PZT–Fe powder compacts as a function of temperature. PZT starts to densify at 750 °C and reaches about 95% of theoretical density at 930 °C. Such sintering behaviour has already been observed and explained in.[1] After sintering at 1000 °C, 1 h the density of PZT ceramics is 7.58 g/cm$^{-3}$. In contrast, both PZT–Fe and PZT–Nb compacts start to densify almost 250 and 350 °C higher, respectively. The densities of PZT–Nb and PZT–Fe ceramics after 1 h at 1100 °C are 7.28 and 6.26 g/cm$^3$, respectively. The results are in contrast with the sintering behaviour of PZT ceramics prepared by mixed-oxide synthesis. While the stoichiometric undoped PZT continuously densifies from 900 to 1200 °C, Nb-doped PZT ceramics with more than 1 at.% Nb densify intensively around 800 °C (occurrence of eutectic composition between lead and niobium oxides),[3] then again above 1100 °C.[4] The occurrence of a liquid phase is also expected in the case of iron doping.[5] By mixed oxide synthesis dense ceramics are prepared at/above 1100–1150 °C, depending on the powder processing conditions.[6]

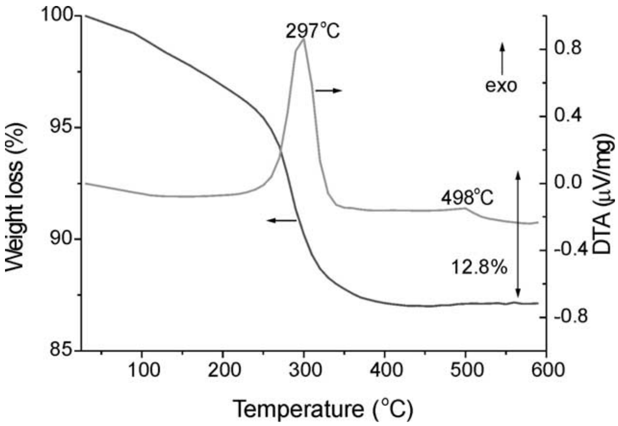

Fig. 1. TG/DTA curves of the as-dried amorphous precursor PZT powder.

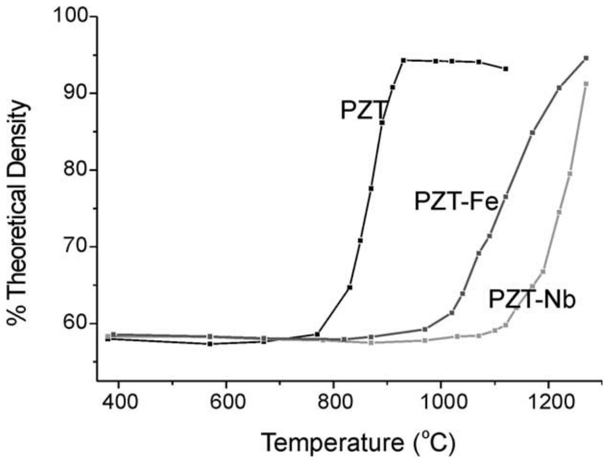

Fig. 2. Sintering curves of PZT, PZT–Nb and PZT–Fe compacts. Density is calculated from the compact densities and shrinkages and expressed as a percentage of theoretical density. The value 8.00 g/cm$^3$ was taken for all three materials.

Both PZT–Nb and PZT–Fe ceramics after sintering at 1100 °C, 1 h consist only of the perovskite phase as determined by XRD (Fig. 3). Microstructural analysis of both PZT–Nb and PZT–Fe provided further information. PZT–Nb reaches 91% of theoretical density, the average grain size is 1.2 μm (Fig. 4a). TEM analysis revealed the presence of submicrometre-sized intragranular pores (Fig. 4b), ferroelectric domains and crystallographic defects (Fig. 4c). No second phase inclusions were found. The origin of the pores is not clear yet.

PZT–Fe consists of submicrometer sized grains with intragranular pores (Fig. 4d). TEM analysis (Fig. 4e) confirmed the presence of up to 100 nm sized intragranular spherical pores. The domain structure of PZT–Fe is finer and more complicated than that of PZT–Nb. 200 nm sized zirconia particles are determined by EDS analysis, located either inside the matrix PZT grains or in the triple junctions. A lead-rich phase containing iron was also determined by EDS at a matrix grain junction

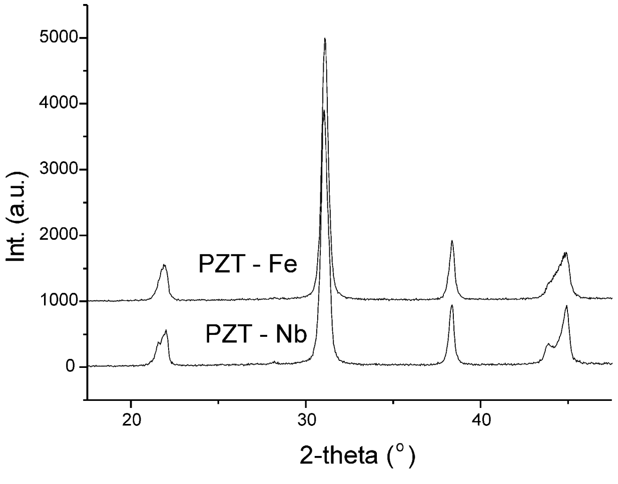

Fig. 3. XRD spectra of PZT–Nb and PZT–Fe ceramics sintered at 1100 °C for 1 h.

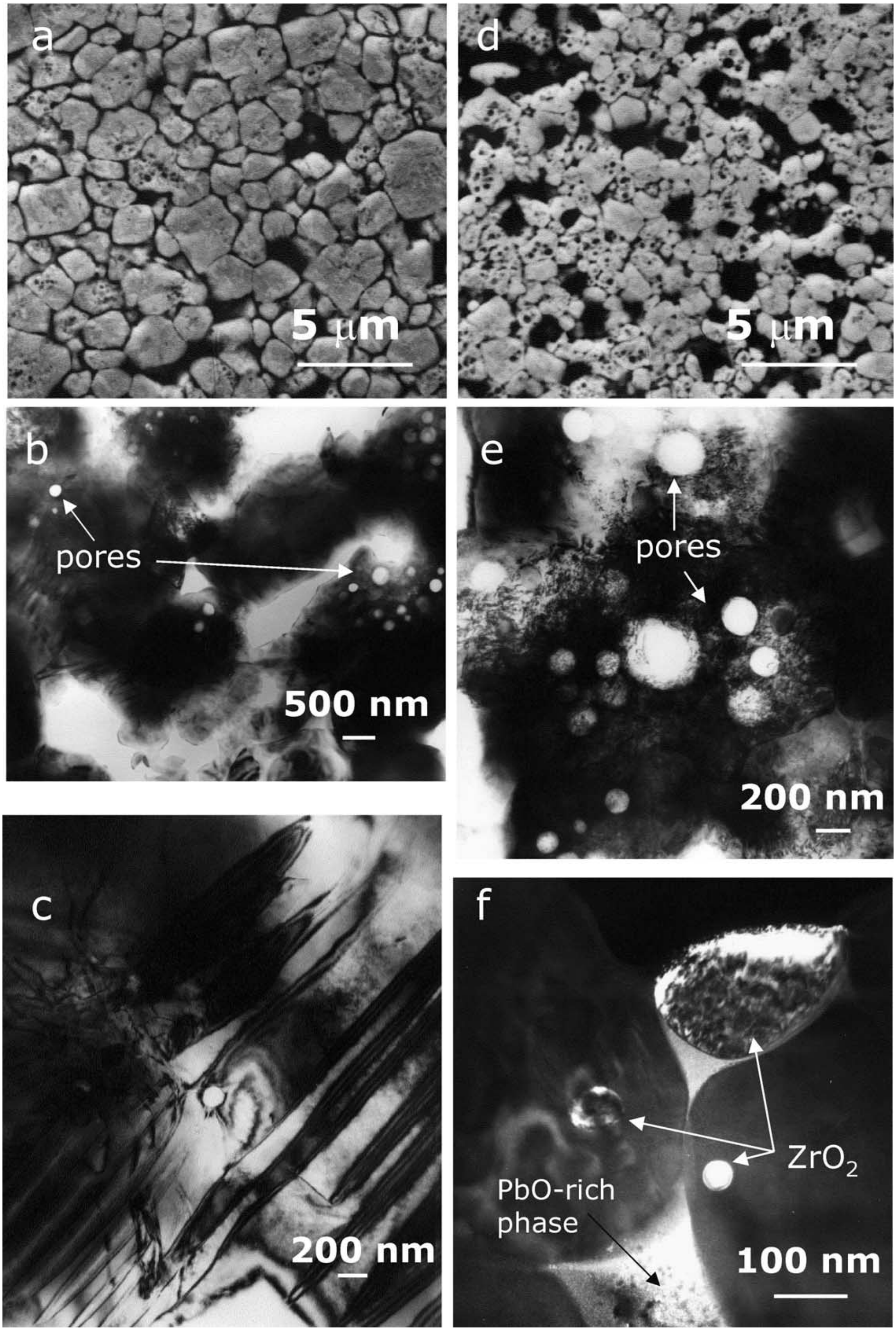

Fig. 4. Microstructural features of PZT–Nb and PZT–Fe ceramics sintered at 1100 °C for 1 h: (a) etched surface of PZT–Nb (SEM), (b,c) TEM micrographs of PZT–Nb, (d) etched surface of PZT–Fe (SEM), (e,f) TEM micrographs of PZT–Fe.

(Fig. 4f). The presence of both zirconia particles and lead-rich phase in iron-doped PZT prepared by mixed-oxide synthesis has been explained by Fernandez et al. Namely, the observed microstructural features are a consequence of iron incorporation into the PZT lattice accompanied by precipitation of zirconia particles and formation of PbO-rich liquid phase.[7]

## 4. Summary

Stoichiometric niobium and iron doped PZT 53/47 ceramics were prepared by alkoxide based solution processing. Incorporation of dopants does not influence noticeably thermal decomposition or crystallisation of the perovskite phase, but has a strong impact on the sintering behaviour: the onset of shrinkage is increased by 250 and 350 °C for niobium and iron doped PZT ceramics, respectively, in comparison to PZT. Detailed microstructural analysis of niobium doped PZT revealed only the presence of a perovskite phase while local heterogeneities on the level of a few 100 nm are present in the iron doped material. Therefore, it is concluded that although homogeneity in the starting iron-doped PZT powder may be achieved by sol-gel processing it is lost by reactions taking place upon sintering.

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