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Hydrothermal Synthesis of Lead Zirconium Titanate (PZT) Powders and their Characteristics

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Abstract

The combined influences of KOH initial concentration and initial lead precursor excess on the characteristics (morphology, powder density, specific surface area, crystalline structure and powder chemical composition) and sintering behaviour of hydrothermally synthesised powders, have been investigated. Optimised conditions (low KOH concentration and presence of lead excess in the feedstock) have been determined that lead to fine deagglomerated and reactive PZT powders densifying at about 850°C. A Pb-rich surface layer has been identified over the grains, that is responsible for this low sintering temperature. Despite the large excess of lead, the core of powders remains lead deficient. But by lowering [KOH]$_o$, it is possible to keep the lead deficiency within a few percent. © 1999 Elsevier Science Limited. All rights reserved

Keywords: chemical composition, powders-chemical preparation, precursors-organic, sintering, PZT.

1 Introduction

In the hydrothermal system, synthesis reactions and growth mechanism of PZT crystals remain unclear. Most of the literature focuses on the achievement of a good chemical composition. For Barsukova *et al.*,[1] the large chemical heterogeneity observed in the grown crystals seems to be influenced by the initial composition of nutrient and growth conditions. Lencka *et al.*[2] reported that PZT formation is governed by he homogeneity of precursors mixture. They determined a thermodynamical domain of stability providing the high yield precipitation of a pure PZT phase, at a temperature as low as 160°C. High reagent concentrations and a basic media (pH 9–14) are required. Cheng *et al.*[3] reported that a high KOH initial concentration allows a very good chemical homogeneity within the powder, provided that an excess of lead precursor is initially introduced to compense lead redissolution in the basic media.

More recently, Su *et al.*[4] produced PZT powders at high temperature (about 300°C), under a relatively high pressure (140 bar), and low KOH concentration (0·4 and 0·8 M). They reported that different mechanisms of PZT formation can occur, depending on the initial mineraliser concentration and pH condition. In several conditions, PZT is mainly obtained via an in-situ mechanism where lead, firstly adsorbed on the precipitate particles, diffuses into the zirconium titanate network, inducing structural rearrangements.

Those considerations allow to establish a non exhaustive list of processing parameters that control the final powder estate: media basicity, reagents concentration, temperature of treatment, nature of precursors and mineraliser. But literature is poor in investigations on how these parameters influence powder characteristics (other than chemical homogeneity), and their sintering behaviour. This has been attempted in this paper, by considering two of the main parameters: the KOH initial concentration and the lead precursor initial excess.

2 Experimental

A clear solution of mixed titanium isopropoxide and zirconium propoxide is prepared in isopropanol. Once hydrolised, it is filtered to eliminate alcohols. The fresh precipitate is then redispersed in

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water. An aqueous solution of lead nitrate is added, in stoichiometric amount or with an excess of 100 mol%. KOH pellets are then introduced: initial KOH concentration, $[KOH]_o$, ranges from 1 to 10 mol l^{-1}, with a pH media of 14. The 650 ml of feedstock should theoretically provide 0·13 mol of PZT. Hydrothermal treatment is performed for 2 h at 265°C, under autogenerated pressure. After the treatment, powder is filtered, washed three times [(i) with distilled water, (ii) with a 10 vol% aqueous solution of acetic acid, to remove unreacted lead oxide, (iii) with distilled water], and oven dried.

3 Characterisaton

Powders were characterised by means of SEM observations (Jeol JSM-T330A), density (Micromeritics Pycnometer 1305), specific surface area measurements (Micromeritics Flowsorb II 2300), X-ray diffraction (Siemens D5000), X-ray fluorescence (Fisons ARL 8410 Sequential) and XPS analyses.

Dilatometric curves were performed at 5°C min^{-1}, from 20 to 1300°C, under a protective atmosphere to prevent lead volatilisation. Densities of sintered samples were determined by the Archimedes method and microstructures observed by SEM after chemical etching.

4 Results and Discussion

The conditions for powder preparation, and powder characteristics are reported in Table 1. The influence of $[KOH]_o$ has been studied through the series 1 (powders A to E), and the influence of initial lead excess has been studied by comparing powders A, D and F, G.

4.1 X-ray diffraction and chemical composition

All X-ray diffraction patterns correspond to pure and well crystallised PZT powders, composed of both tetragonal and rhombohedral phases. But chemical composition of crystalline phases is distributed on either side of the expected morphotropic stoichiometry: the perfect homogeneity can not be achieved.

The global chemical composition of powders has been measured by X-ray fluorescence, through molar ratios. Lead zirconium titanate can then be expressed as $Pb_R\ (Zr_XTi_{(1\text{-}X)})O_{2+R}$.

Although powders exhibit a ratio X close to the feedstock composition, R is lower than 1 for most of them, meaning they are lead deficient. At $[KOH]_o = 1$ M, powder F is more deficient ($R = 0·91$) than powder A ($R = 0·96$). Lead excess compensates the lead deficiency of powders, but remains insufficient to achieve the theoretical stoichiometry.

Within 2 to 4 mol% at low $[KOH]_o$, lead deficiency reaches about 12 mol% at 10 M, in powders of series 1. A substitution of lead by potassium could be at the origin of this deficiency. However, EDS analyses did not reveal any trace of K^+.

4.2 Powders morphology (Fig. 1)

At $[KOH]_o = 1$ M, particles are cubic shaped. The calculated mean diameter, Φ_{BET}, of powder A and F is, respectively, of 0·46 and 0·26 μm. Powder A, prepared through the lead excess process, is more deagglomerated.

Above 2 M, powders B to E exhibit micrometric particles, composed of fine piled up platelets. They are more facetted as $[KOH]_o$ increases. A mechanism of secondary nuleation on primary nuclei may have occurred, probably enhanced by increasing $[KOH]_o$.

Assuming a theoretical value of 8 g cm^{-3}, relative powder density, in series 1, decreases gradually from 98% at 1 M, to 91% at 10 M (Fig. 2). Formation of an amorphous phase would imply that specific surface area increases with $[KOH]_o$. But it decreases from 1·66 m^2 g^{-1}, at 1 M, to a stable mean value of 0·5 m^2 g^{-1} above 2 M. These evolutions can only be explained by the formation of entrapped porosity.

At low $[KOH]_o$, lead excess in the feedstock seems to favour crystals coarsening: Φ_{BET} of powder A is higher than powder F (0·46 against 0·26 μm), which is confirmed by SEM observations. Influence

Table 1. Hydrothermal conditions followed for powders preparation and powder characterists

	Powders denomination	*$[KOH]_o$ (mol l^{-1})*	*Initial lead precursor excess (mol%)*	X *(%)*	R *(%)*	ρ *(g cm^{-3})*	S_{BET} *(m^2 g^{-1})*	Φ_{BET} *(μm)*
Series 1	A	1	100	52	96	7·91	1·66	0·46
	B	2	100	53	98	7·83	0·57	1·35
	C	3	100	51	100	7·86	0·39	1·96
	D	5	100	50	104	7·71	0·61	1·29
	E	10	100	52	88	7·26	0·47	1·74
Series 2	F	1	0	50	91	7·67	3·07	0·26
	G	5	0	53	65	6·89	12·66	0·07

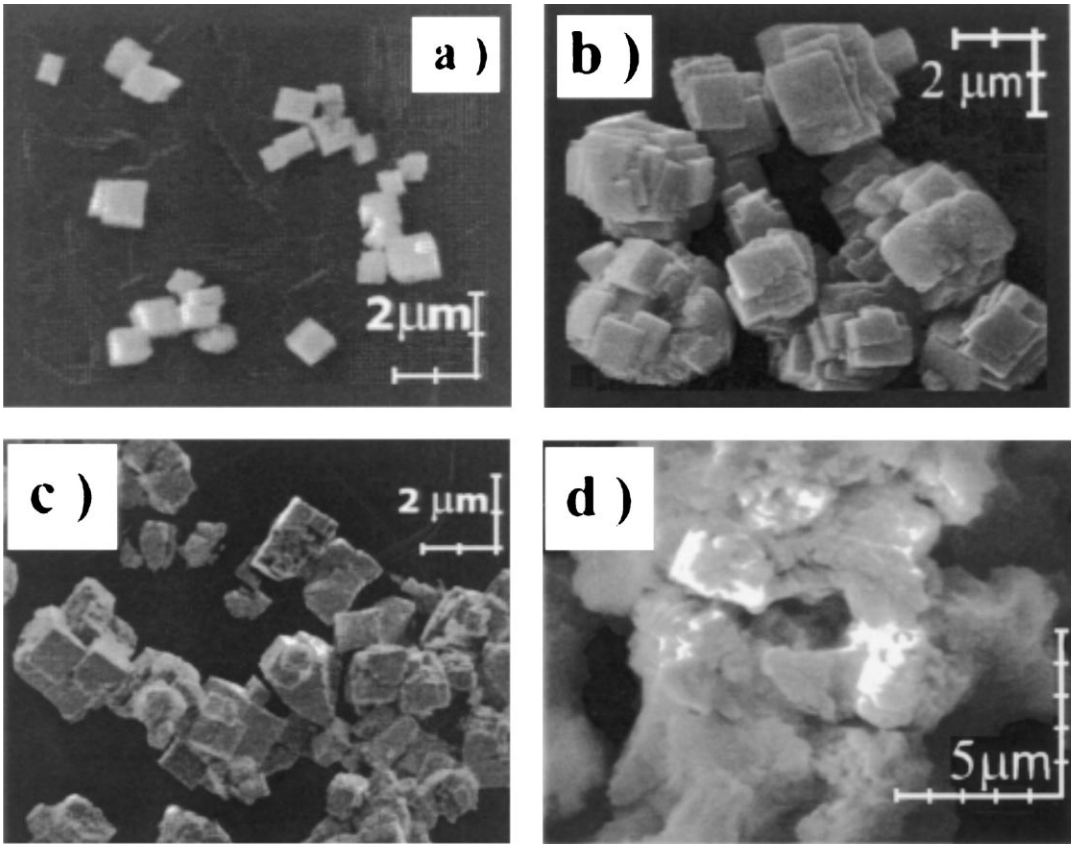

Fig. 1. Powders morphology: (a) Powder A: $[KOH]_o = 1$ M, initial lead excess 100 mol%; (b) Powder D: $[KOH]_0 = 5$ M, initial lead excess 100 mol%; (c) Powder F: $[KOH]_o = 1$ M, no initial lead excess; (d) Powder G: $[KOH]_o = 5$ M, no initial lead excess.

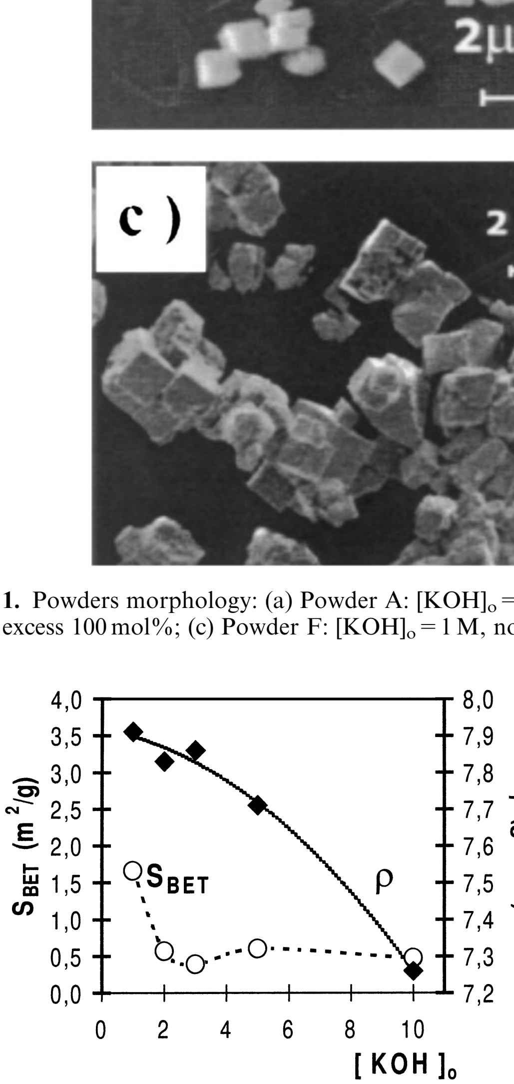

Fig. 2. Evolution of powder density and specific surface area versus $[KOH]_o$ in the lead excess process.

of lead excess is more noticeable at higher $[KOH]_o$. Powder G [$\rho = 6{\cdot}89$ g cm^{-3}, $S_{BET} = 12{\cdot}66$ m^2 g^{-1}, $\Phi_{BET} = 0{\cdot}07\,\mu$m) has a cloudy morphology (Fig. 1) while powder D ($\rho = 7{\cdot}71$ g cm^{-3}, $S_{BET} = 0{\cdot}61$ m^2 g^{-1}, $\Phi_{BET} = 1{\cdot}29\,\mu$m] is well facetted.

4.3 Sintering behaviour (Figs 3 and 4)

For powders B to G, samples are fully densified above 1250°C.

When the ratio $[KOH]_o/[Pb(NO_3)_2]_o$ is too high (powders E and G), a dedensification occurs at about 1250°C leading to some large open porosity observed in microstructures but not to grain coarsening.

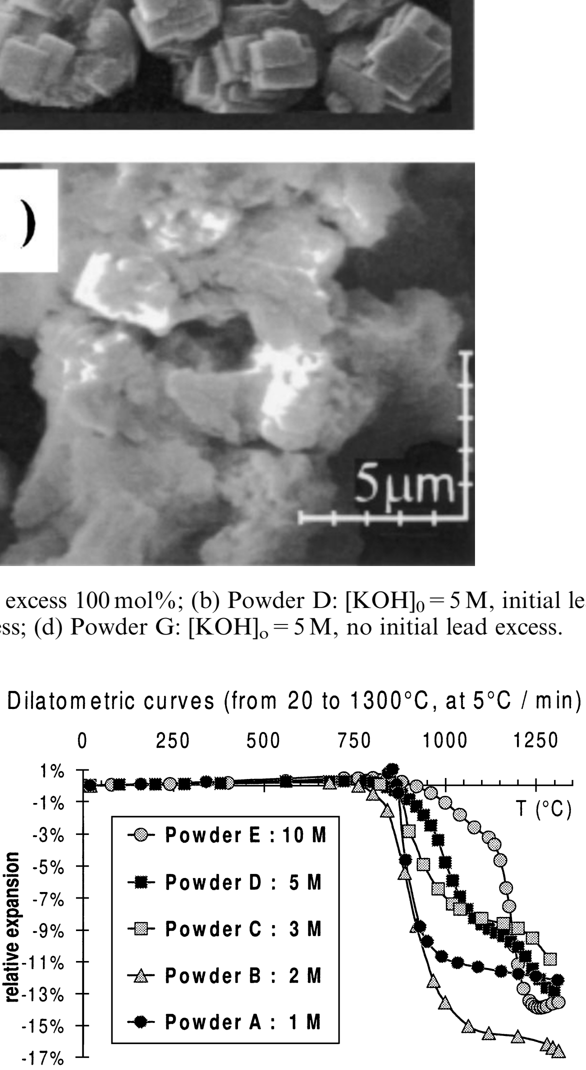

Fig. 3. Influence of $[KOH]_o$ on sintering behaviour, in the lead excess process.

Powders B to E exhibit a two-step densification behaviour. A self shrinkage of fine piled up platelets may occur in a first time, leading to bigger particles. Those particles would then sinter together during the second step.

Powder A (100% lead excess) is by far the most reactive. Sintering occurs in one step at 850°C and full densification is achieved at 950°C, while powder F (no lead excess) requires a much higher sintering temperature (above 1250°C). Such a shift of sintering temperature is usually observed, in traditional processes, when lead oxide is employed as a sintering aid: densification occurs in the same range of temperature (850–950°C) while a transient liquid phase sintering mechanism is involved.

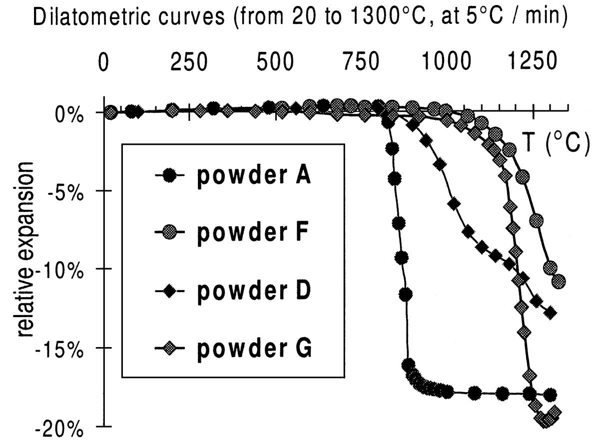

Fig. 4. Influence of lead excess on sintering behaviour at $[KOH]_o = 1$ and 5 M.

XPS analyses were performed on pellets of an A-type and a F-type powder. Intensity of the lead signal, is higher in the case of powder A. Chemical shifts of signal position indicates that lead oxidation state is closer to Pb_3O_4 for powder A while it is closer to PbO for powder F. After 10 min of ion etching, powder F still exhibits the same signal. For powder A, the signal decreases in intensity and shifts to lower energies; lead oxidation state is then close to PbO. Both powders seem to have the same core composition, but in the lead excess hydrothermal process, a Pb-rich layer is formed over the grains, where lead oxidation state is close to Pb_3O_4. This surface layer could be at the origin of sintering temperature lowering.

5 Conclusion

The influence of KOH initial concentration on powders characteristics and sintering behaviour has been studied in association with the influence of initial lead excess.

Powders are fine, pure and well crystallised directly after the hydrothermal treatment. Both tetragonal and rhomboedral phases coexist within the powder, but the perfect composition homogeneity can not be achieved. However, further homogeneisation occurs during sintering.

The global ratio X of powders is well controlled, but the grain core is lead deficient. The introduction of lead excess compensates this lead deficiency by forming a Pb-rich surface layer over the grains, in which Pb oxidation state is close to Pb_3O_4. In addition, an increase of $[KOH]_o$ involves lead redissolution in the media, increasing the lead deficiency.

Powders morphology is closely related to the effects of $[KOH]_o$ and initial lead excess, and seems to influence the powder sintering behaviour.

Lead excess favours the achievement of a good crystallisation. At $[KOH]_o = 1$ M, particles are cubic shaped, with a submicron size, and densify in one step. Above 1 M, a secondary nucleation mechanism on primary nuclei appears, which is enhanced by increasing $[KOH]_o$. Simultaneously, entrapped porosity is formed. Particles are then composed of fine piled up platelets. This morphology could be responsible for their two-step densification behaviour.

At 1250°C, a dedensification occurs when the ratio $[KOH]_o/[Pb]_o$ is too high, involving some large open porosity but no grain coarsening is observed.

At $[KOH]_o = 1$ M, the Pb-rich surface layer formed over the grains in the lead excess process, is responsible for the powders high reactivity. Samples are fully densified at 950°C. A mechanism of transient liquid phase sintering can be expected.

At such a low sintering temperature, lead volatilisation is very limited: dense material is then expected to have the same chemical composition as the powder, the slight lead deficiency would only come from the hydrothermal process.

Acknowledgements

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