

Mechanism of PZT crystallisation under hydrothermal conditions Development of a new synthesis route

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Abstract

On the basis of a 1-stage hydrothermal process, we first investigated the reaction mechanism responsible for the PZT precipitation. In a first sequence, lead diffuses into the amorphous coprecipitate. By increasing the reaction temperature, these particles dissolve, leading to nucleation and growth of PZT well faceted particles. In a second step, we demonstrated that starting from very fine oxide precursors, a homogeneous PZT solid solution could be formed. Under the same conditions but without any lead precursor, a mixture of KTO (a potassium titanium oxide phase) and tetragonal zirconia is formed. A 2-stage process was developed on these assumptions. The first stage consists in producing the KTO–ZrO₂(T) mixture. In the second stage, this mixture is hydrothermally treated in presence of lead precursor. Pure and homogeneous PZT and PLZT powders were obtained throughout this new synthesis route. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical composition; Crystallisation mechanism; Dopant integration; Hydrothermal; Lanthanum; Powders-chemical preparation; Precursors-organic; Precursors-oxides; PLZT; PZT

1. Introduction

Usually, the hydrothermal synthesis of PZT powders is based on a 1-stage process: a mixture containing all the precursors is prepared and treated once under hydrothermal conditions. We previously developed such a process¹ starting from organic precursors. However, when trying to synthesise PLZT powders we observed that lanthanum, instead being integrated within the PZT network, forms needles by reacting separately with lead precursor.

On the other hand, the feedstock preparation, easily conductible in laboratories, is hardly adaptable to an industrial production. Indeed, as hydrothermal treatment is applied to a homogeneous mixture of liquid precursors, feedstocks are prepared through different ways to optimise this homogeneity. The most simple is to co-hydrolyse an intimate mixture of zirconium and titanium alkoxides, before adding lead precursor. But alkoxide precursors are expensive and volatile thus difficult to manipulate. Several authors prepare stabilised stock solutions starting from cheaper precursors. This preparation is long and delicate. Moreover, stock solutions have to be regularly controlled because of ageing. For these reasons, hydrothermal processing of PZT is

still unable to compete with the classical mixed oxide route. It is then worth simplifying the hydrothermal process by starting from oxide precursors: easy to manipulate and far cheaper.

For these reasons, we decided to investigate another synthesis route allowing the integration of lanthanum and the use of oxides precursors.

At first, it is necessary to determine the mechanism of PZT crystallisation in hydrothermal conditions, and whether a homogeneous PZT solid solution can be formed starting from a heterogeneous precursor system. This second condition must be satisfied if oxide precursors have to be used. Several papers attempt to describe the reaction mechanism.

Kutty² investigated hydrothermal synthesis starting from a neutral pH feedstock. The hydrothermal treatment was conducted in the temperature range 130–400°C, for 8 h. He proposed the following sequence of reactions: (1) at 130°C a solid solution of titania in a PbO matrix (PbOss) crystallises; (2) PbOss reacts with the amorphous species to give an amorphous PZT solid solution; (3) upon increasing the reaction temperature, the amorphous PZT crystallises while X-ray reflections of PbOss decrease. Temperature must be at least of 300°C to obtain a phase pure PZT powder.

Cheng et al.³ observed the formation of PbOss within the amorphous particles of hydrous titania (in-situ

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mechanism), as soon as 120°C. Upon increasing temperature PbOss disappears on behalf of PZT formation. From 150 to 220°C, they observed the homogenisation of PZT solid solution. The effect of KOH initial concentration was also investigated for powders processed for 2 h at 250°C. At 1 mol/l, PZT powders exhibit some chemical heterogeneity. Particles are cubic shaped with a submicrometric size. An increase of $[KOH]_0$ induces the homogenisation of the solid solution as well as a change in morphology. At 5 mol/l, particles are rounded with a nanometric size. This result is consistent with a dissolution–precipitation mechanism.

Su et al.⁴ performed the hydrothermal treatment at 350°C for 6 h. TEM micrographs reveal that up to 250°C crystallisation seems to proceed via collapse of the amorphous gel. PbOss crystallites are detected as well as very fine acicular PZT particles. After synthesis at 300°C for 2 h, PZT powders with a cubic morphology are formed. The isoelectric point (IEP) was determined for powders sampled during and after the hydrothermal treatment. As temperature increases from 250 to 300°C, IEP decreases from pH 10 (close to IEP of PbO) to pH 6.5 (close to IEP of crystalline zirconium titanate). They conclude that PZT crystallisation occurs mainly via an in-situ mechanism, where lead diffuses into the amorphous zirconium titanate which then condenses through the expulsion of water. A slight dissolution and recrystallisation is observed in the later stage of the process.

It appears clearly that a change of synthesis conditions modifies the reaction mechanism. However, PZT formation always seems to happen through a combination of an in-situ and a dissolution–precipitation mechanisms. In our experimental conditions, we can expect to observe both these phenomena, but we have to find in which way they participate to the achievement of a homogeneous PZT solid solution.

2. Experimental

In the 1-stage route, a clear solution of mixed titanium and zirconium alkoxides is prepared in isopropanol. This solution is hydrolysed and filtered. The fresh precipitate is then redispersed in water and mixed with an aqueous solution of lead nitrate. The basicity of the medium is adjusted by introducing KOH pellets. After the hydrothermal treatment, the crystalline powder is filtered and washed with water. When an excess of lead precursor is introduced, two additional washings (i) with a dilute acetic acid solution, (ii) with water, are realised to remove the unreacted lead. This acidic treatment was also applied to remove the adsorbed lead species.² After this acidic washing, only the chemically combined lead remains within the powders.

On the basis of the 1-stage process, the investigation of the reaction mechanism and the development of the

second hydrothermal route were performed starting with different systems of precursors. A mixture of Zr-rich PZT and lead titanate powders is produced through the 1-stage organic based process. Crystalline oxide precursors consist in litharge PbO (Metaleurop, mean diameter of 4 µm), rutile/anatase TiO₂ (Criceram, mean diameter of 0.2 µm), nanosized anatase TiO₂ (P25, Degussa), monoclinic ZrO₂ (MEL Chemical Magnesium, mean diameter of 0.9 µm). Amorphous hydrous titania and zirconia were produced by the hydrolysis of titanium tetraisopropoxide and zirconium tetrapropoxide.

3. Characterisation

Powders were characterised by means of SEM-EDX analysis (Jeol JSM-T330A), X-ray diffraction (Siemens D5000), X-ray fluorescence (Fisons ARL 8410 Sequential), ICP spectrometry (Jobin Yvon 38 S), TGA-DTA thermal analysis (Setaram TG-DTA 92), specific surface area measurements (Micromeritics Flowsorb II 2300), He-pycnometry (Micromeritics Pycnometer 1305). The relative density was calculated assuming a theoretical density of 8.

4. Results and discussion

4.1. Approach to the crystallisation mechanism in the 1-stage hydrothermal process

The powder prepared at 140°C from zirconium and titanium alkoxides and lead nitrate is X-ray amorphous. No PbOss phase is thus detected. This powder exhibits the same morphology as zirconium and titanium coprecipitate (Fig. 1). To remove any unreacted and adsorbed lead species, this powder was subjected to an acidic washing. EDS spectra captured before and after washing reveal a decrease of intensity for the peak related to lead. TGA-DTA traces before and after acidic washing are illustrated in Fig. 2. The weight loss in the range 200–400°C is due to the removal of adsorbed hydroxyl groups. An exothermic peak appears at 300°C. XRD pattern for the powder calcined at 400°C does not reveal any detectable crystalline phase. As the hydrothermal synthesis is performed on an aqueous medium, this peak cannot be attributed to the oxidation and the removal of organics. Therefore, it may originate in a rearrangement of the network leading to the nucleation of crystallites. The exothermic peak at 540°C corresponds to the formation of PZT phase. After acidic washing, these peaks are shifted respectively to 340 and 660°C.

The powder synthesised at 160°C was also acid washed. This powder exhibits a high value of the specific surface area (175 m²/g) and a low relative density (51%). PZT reflections appear on XRD pattern, but the

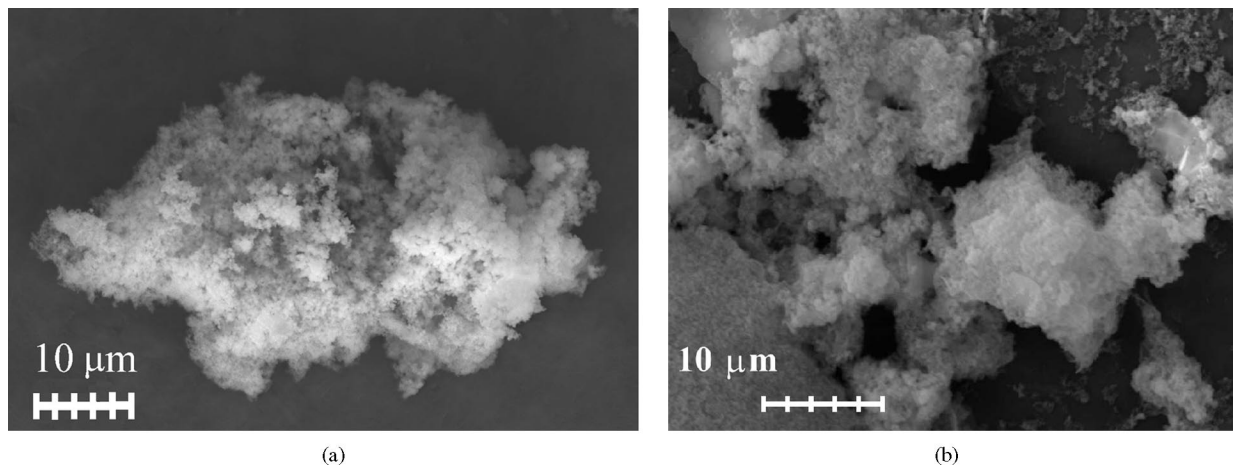


Fig. 1. (a) Typical morphology for the coprecipitated particles. (b) Typical morphology for the powder synthesised at 140°C for 2 h.

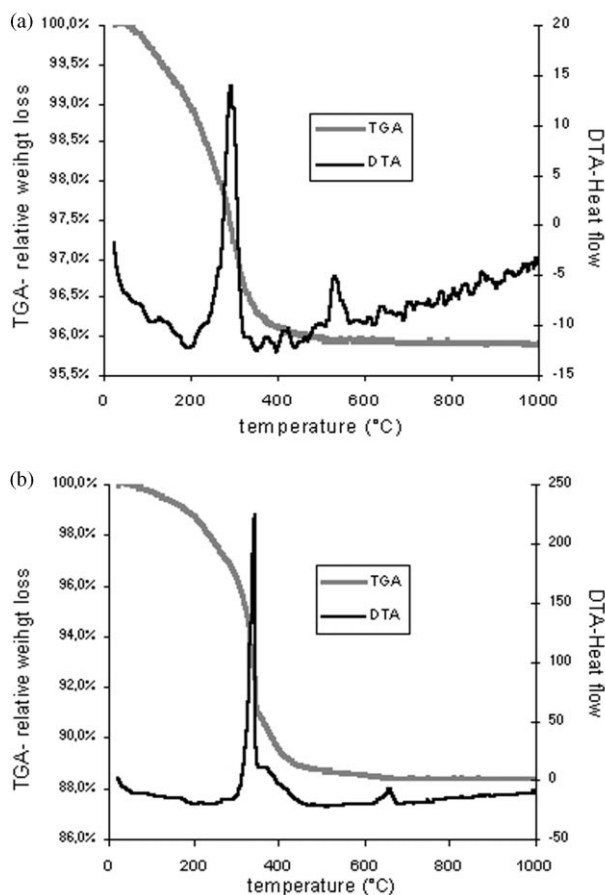


Fig. 2. TGA–DTA traces for the powder synthesised at 140°C for 2 h. (a) Before acidic washing. (b) After acidic washing.

powder remains partially amorphous. The two exothermic DTA peaks are still observed at 330 and 640°C. SEM observations reveal mainly two kinds of particles. The A-type particles correspond to large agglomerates composed of nanosized grains (Fig. 3a). They exhibit the same aspect as coprecipitate or powder synthesised

at 140°C. EDS analysis reveals some lead deficiency in comparison with PZT crystals. The B-type cubic shape particles have a micrometric size (Fig. 3b). They can be either isolated or agglomerated. The EDS spectrum is typical of PZT phase.

Powders synthesised from 180 to 265°C are fully crystallised. No DTA-peak is observed. The weight loss still occurs between 200 and 400°C. As the synthesis temperature increases, powder density remains unchanged (96–97%) and no significant change for the specific surface area is observed. The change of morphology is illustrated in Fig. 4. In the range 180–190°C, a higher proportion of well faceted and cubic shape particles (B-type) is observed. Several A-type agglomerates are still present. Powders synthesised at 265°C are only composed of B-type particles. It is noteworthy that powders synthesised in the range 180–265°C exhibit the same chemical homogeneity.

This first series of results allows a global view of the mechanism.

At 140°C, lead is mostly adsorbed on the particles surface. A fraction has diffused into the coprecipitated network, but the powder remains X-ray amorphous. No PbOss is detected. At 160°C the powder is partially crystallised. It is composed of a large amount of A-type particles and a small amount of B-type particles. A-type particles are lead deficient and exhibit the same morphology as Zr–Ti coprecipitate. B-type particles exhibit an EDX spectrum typical of PZT solid solution and are well faceted with a cubic shape and a micrometric size.

In an in-situ crystallisation mechanism, there is a correlation between the particle size of the amorphous phase and crystals. Crystals and amorphous particles exhibit the same aspect. On the contrary, this correlation does not exist in a dissolution–precipitation mechanism. A-type particles are produced by the diffusion of lead species into the network of the coprecipitated particles. B-type particles are produced through a dissolution–precipitation

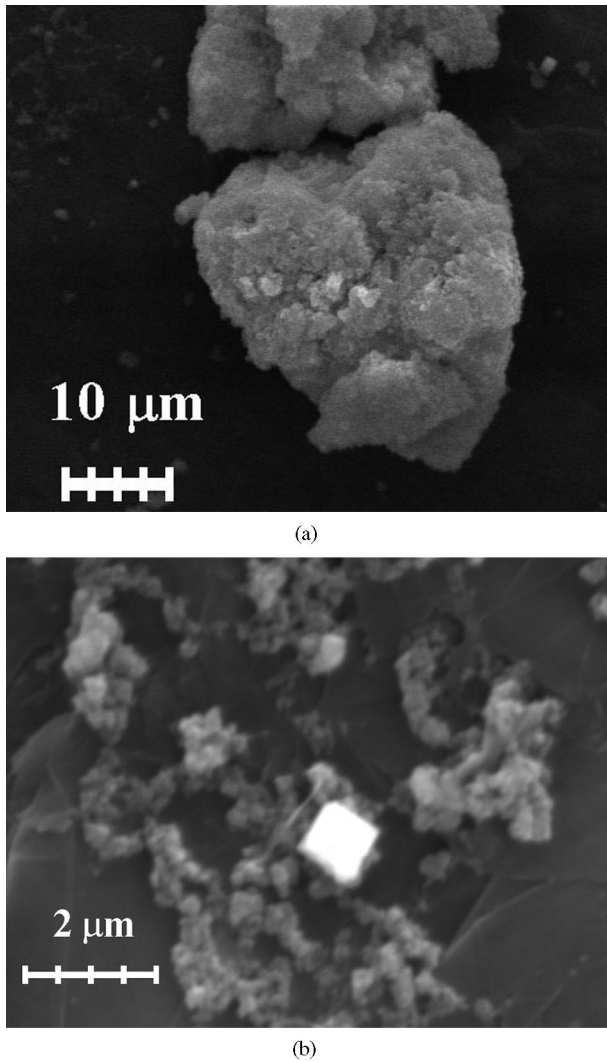


Fig. 3. Morphology of the powder synthesised at 160°C for 2 h. (a) A-type particles. (b) B-type particle.

mechanism. Upon increasing the reaction temperature, the proportion of B-type particles increases. At 265°C, no A-type particle is observed.

We assume that in these hydrothermal conditions, PZT precipitation occurs mainly by the following route. Before the hydrothermal treatment, lead species are adsorbed on the Zr–Ti coprecipitated particles. During the hydrothermal treatment, lead diffusion into the coprecipitate induces the formation of A-type particles. This mechanism is predominant at low temperature. Then, as temperature increases, A-type particles dissolve, leading to nucleation and growth of B-type particles.

As A-type particle dissolution has been demonstrated, the study of the mechanism was pursued to determine whether B-type particles also dissolve inducing a further homogenisation of the solid solution. In that frame, two feedstocks were prepared starting either from fine Zr-rich PZT, amorphous hydrous titania and lead nitrate,

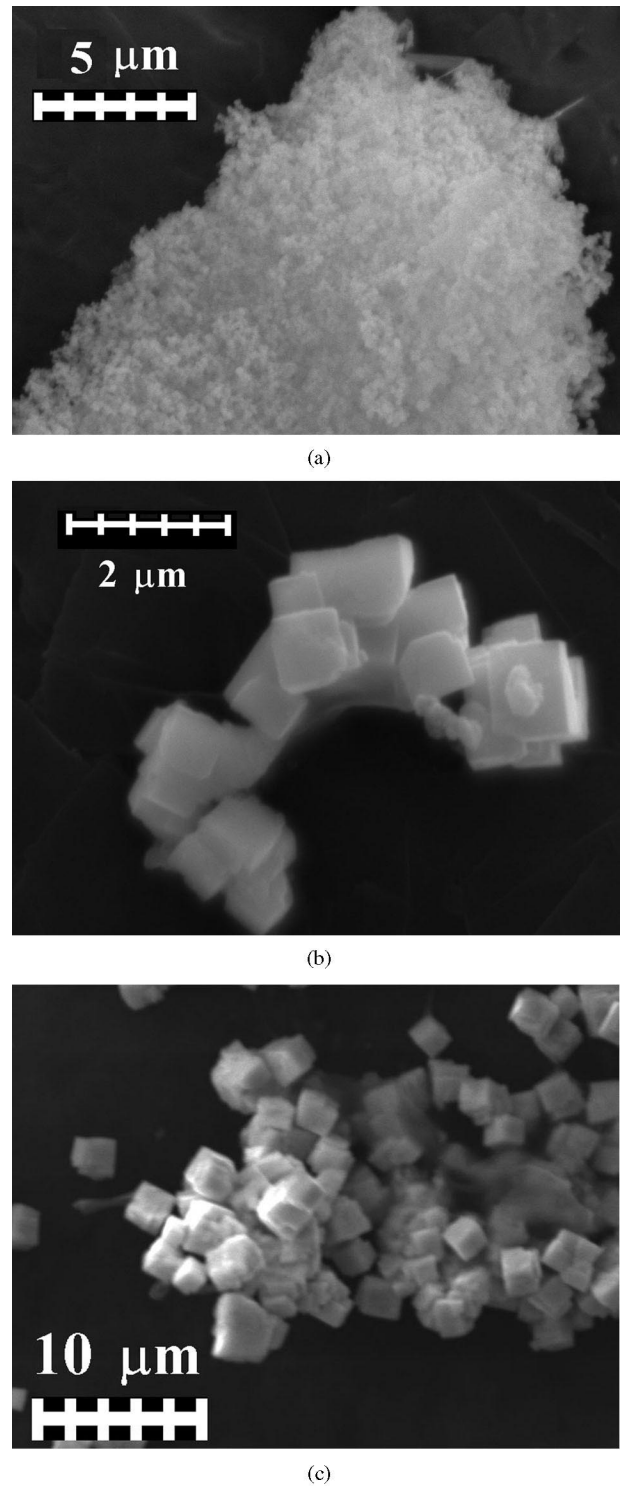


Fig. 4. Change of morphology with increasing the treatment temperature. (a) A-type particles (powder synthesised at 190°C). (b) B-type particles (powder synthesised at 180°C). (c) B-type particles (powder synthesised at 265°C).

or from nanosized lead titanate, amorphous hydrous zirconia and lead nitrate. These heterogeneous precursor systems were selected to represent a mixture of A-type and B-type particles corresponding to an intermediate

state of the medium in the sequence of reaction. Heterogeneous B-type particles correspond to the perovskite type precursor, while heterogeneous A-type particles are formed during the beginning of hydrothermal treatment as lead diffuses into the amorphous hydrous precursor.

The hydrothermal treatment was conducted at 265°C for 2 h. This temperature is assumed to be sufficiently high to favour the dissolution–precipitation mechanism. As this mechanism is probably enhanced by increasing the KOH initial concentration,³ $[\text{KOH}]_0$ was fixed at 5 mol/l. When treated in such a highly basic medium, final powders are highly lead deficient. An initial excess of 100 mol% of lead precursor was employed to limit this deficiency.

Therefore, two phenomena can be expected: either the dissolution of fine perovskite type particles giving rise to the nucleation and growth of homogeneous PZT, or the growth of the as-introduced particles leading to a heterogeneous final powder.

XRD data indicate that final powders are highly heterogeneous. Thus, if any dissolution of B-type particles occurs, it is negligible so that no rehomogenisation is achieved. To produce a homogeneous PZT solid solution, the limiting step corresponds to the formation of reactive intermediate species that dissolve with increasing the reaction temperature. In our first system, these species consisted of A-type particles formed via the diffusion of lead in the amorphous precipitate. We assume that such intermediate phases of a different nature can be formed by changing the precursors nature. In that frame, we investigated the possibility to form PZT powders starting from oxide precursors.

4.2. Powder synthesis starting from oxide precursors

According to Lencka and Riman,⁵ the synthesis of a homogeneous PZT solid solution cannot be achieved with separate sources of Ti and Zr. In our case however, hydrothermal conditions are different: the temperature (265°C) is sufficiently high to favour the growing of particles by dissolution–precipitation.

We first attempted to synthesise PZT solid solution from a mixture of coarse oxide powders: PbO, TiO₂ and ZrO₂. To enhance the dissolution mechanism, synthesis was conducted with a $[\text{KOH}]_0$ value of 5 mol/l. Lead precursor was introduced with an excess of 100 mol% to limit the lead deficiency in the final powder.

The reaction product was composed of lead titanate and unreacted zirconia. This observation has already been reported by Lencka and Riman. By replacing crystalline ZrO₂ with a fresh hydrous zirconia (ZrO₂·*n*H₂O), their final powder was composed of lead titanate and lead zirconate. In our conditions, we can expect that lead will diffuse into the precursors particles and induce their dissolution. This dissolution may contribute either

to the chemical rehomogenisation of the medium, or to the growing of lead titanate and lead zirconate crystals. In that second case, we showed previously that neither PbTiO₃ nor PbZrO₃ redissolve sufficiently to give a homogeneous PZT final powder. Evidently, the more precursors are reactive and mixing is achieved at a microscopic scale, the more rehomogenisation should be favoured.

We studied the behaviour of the following heterogeneous precursor systems:

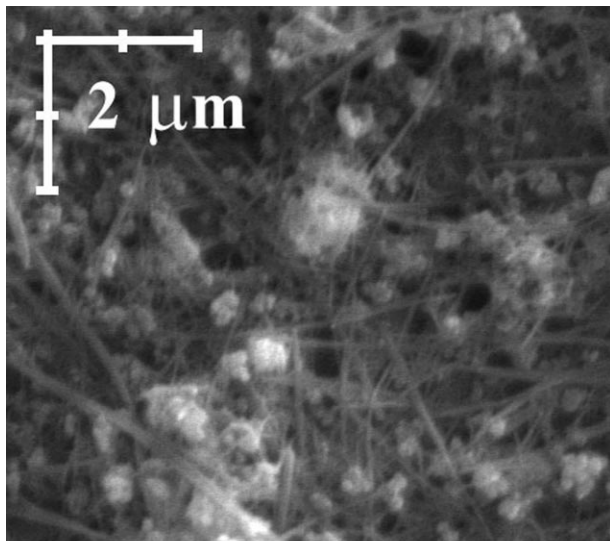
1. PbO, micrometric sized crystalline TiO₂, fresh hydrous zirconia (system 1);
2. lead nitrate, nanosized crystalline TiO₂, fresh hydrous zirconia (system 2);
3. lead nitrate, fresh hydrous titania (TiO₂·*n*H₂O), fresh hydrous zirconia (system 3).

These systems consist of a gradual increase of the precursor reactivity. The hydrothermal treatment was conducted at $[\text{KOH}]_0 = 1$ mol/l and $[\text{KOH}]_0 = 5$ mol/l.

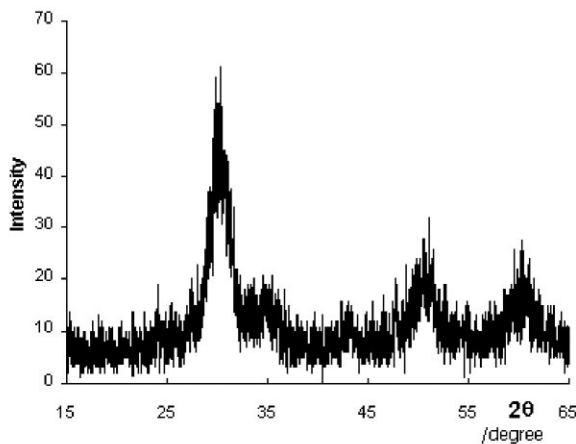
At 5 mol/l, all systems lead to the formation of homogeneous PZT solid solution. PZT particles are well faceted (B-type). At 1 mol/l, only the third precursor system (the most reactive) allowed the formation of PZT. These results can indicate that at 1 mol/l, the growing of PbTiO₃ and PbZrO₃ particles is favoured. A small amount of unreacted titania is X-ray detected when the first system is treated at 1 mol/l. Crystalline titania seems to undergo an attack by KOH. In the system 2, as titania is more reactive, this attack may be total. However, in all previous systems the effect of KOH on zirconium and titanium precursors is simultaneous with the lead-induced reactions. Thus, to distinguish the KOH effect, the previous syntheses were reproduced in the absence of lead precursor. The following systems were thus treated at $[\text{KOH}]_0 = 1$ and 5 mol/l:

1. nanosized crystalline TiO₂, fresh amorphous hydrous zirconia (system 4, derived from system 2);
2. amorphous hydrous titania, amorphous hydrous zirconia (system 5, derived from system 3).

At 5 mol/l, both systems lead to the same reaction product (Fig. 5): tetragonal zirconia, ZrO₂(T), is clearly detectable on XRD patterns. The long fibres, analysed by EDX, are composed of potassium and titanium. This compound, called KTO hereafter, has not yet been identified. When system 4 is treated at 1 mol/l, the mixture of KTO and ZrO₂(T) is obtained. On the contrary, only tetragonal zirconia is formed starting from system 5; the crystalline titania remains unreacted. It is noteworthy that precursors systems and synthesis conditions leading to a homogeneous PZT solid solution are giving KTO. The mixture of KTO and ZrO₂(T) seems to be an intermediate system able to redissolve by reacting with lead precursor.



(a)



(b)

Fig. 5. (a) Mixture of tetragonal zirconia (rounded particles) and KTO (fibres). (b) XRD pattern.

4.3. Development of a new synthesis route: 2-stage process

On the previous assumptions, we developed a new synthesis route based on a 2-stage process. The first stage consists in treating amorphous zirconia and crystalline titania with a KOH initial concentration sufficiently high to attack titania and form the KTO phase. Dopants, like lanthanum can be integrated in the network at this step. After the treatment, the mixture is washed until the achievement of a neutral medium. After the addition of lead precursor, a second hydrothermal treatment is performed. The synthesis conditions ($[\text{KOH}]_0$ and lead initial excess) can be adapted depending on the powders characteristics (sintering behaviour, morphology) to be achieved. Our processing conditions are illustrated in the flow diagram (Fig. 6).

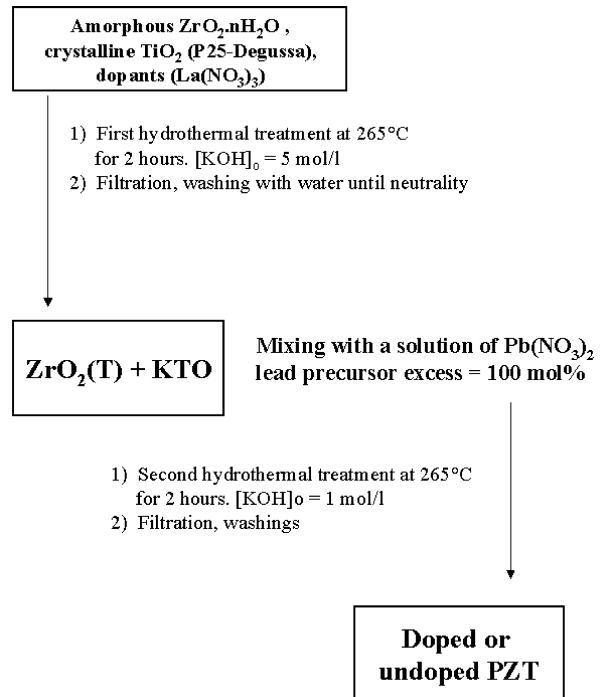


Fig. 6. Flow diagram of the 2-stage synthesis process.

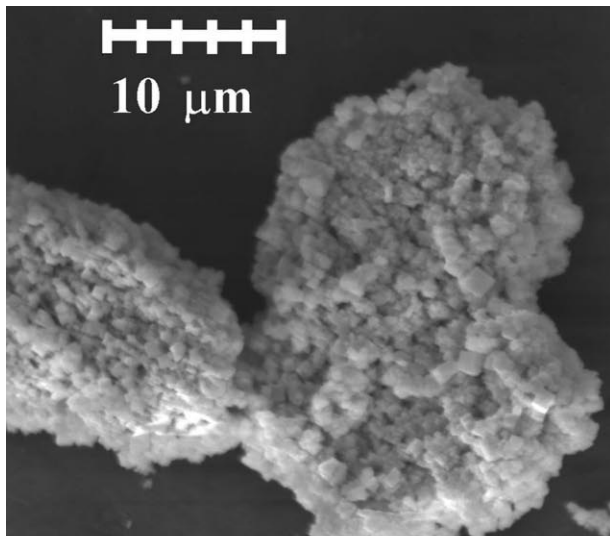
4.3.1. Synthesis of undoped PZT

SEM micrograph and XRD patterns are presented in Fig. 7. The PZT solid solution is homogeneous and phase pure. Powder exhibits micrometric-sized faceted or cubic shape particles (B-type); this morphology is typical of PZT powders prepared through the 1-stage organic-based process under the same conditions. Another kind of particle is also observed: these are large aggregates with nanosized grains arising on the surface.

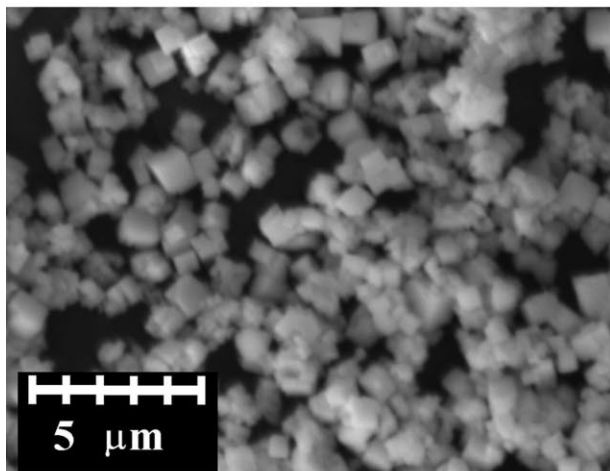
Lead deficiency is higher (12 mol%) than in the 1-stage process under the same conditions (2–4 mol%). This deficiency is responsible for the lower relative density (97% instead of 99%). Potassium pollution of the powder is not sensitive to the change of processing: about 2 mol% of potassium is detected in the powders synthesised either through the 1-stage or through the 2-stage process.

4.3.2. Synthesis of PLZT

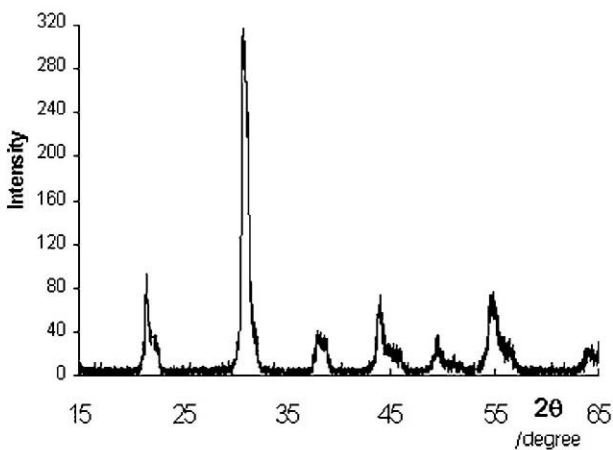
10 mol% lanthanum doped PZT were prepared under the same synthesis conditions through the organic-based 1-stage and the 2-stage routes. For the 1-stage processed powder, X-ray diffractogram reveals the presence of a second phase. These secondary peaks are not sufficiently intense to be attributed. The powder is composed of PZT B-type particles and needles (Fig. 8). EDX analyses indicate that needles are composed of lanthanum and



(a)

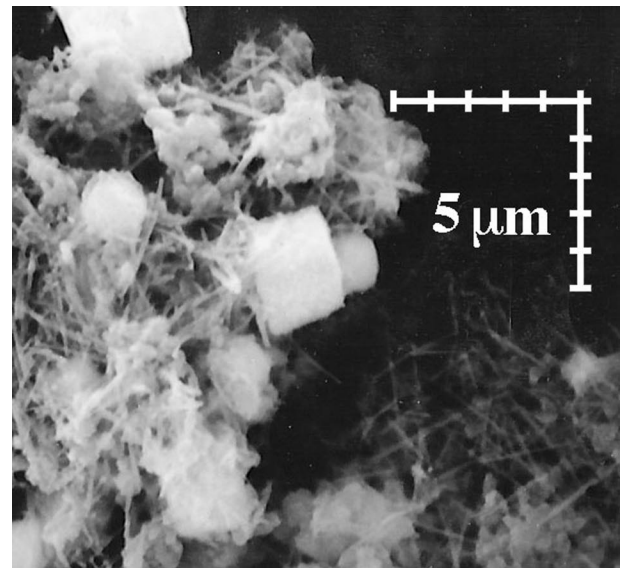


(b)

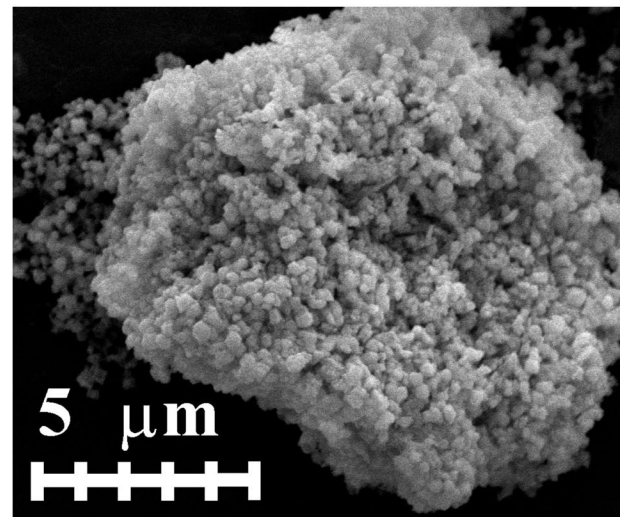


(c)

Fig. 7. PZT powder synthesised at 265°C for 2 h through the second route. (a) Large agglomerates composed of cubic shaped or rounded grains. (b) Cubic shape particles (B-type). (c) XRD pattern.



(a)



(b)

Fig. 8. (a) PLZT processed through the 1-stage organic based route. (b) PLZT processed through the 2-stage route.

lead. These needles are formed even when doping at 1 mol%. Lanthanum reacts separately with lead precursor instead of incorporating the PZT network: the 1-stage route is unfavourable to the synthesis of PLZT powders.

In the 2-stage route, no needles are formed. Lanthanum may have integrated the $ZrO_2(T)$ phase or the KTO fibres during the first sequence of the process. After the second hydrothermal treatment, XRD data are in agreement with JCPDS standard.⁶ EDX analysis indicates that powder is composed of Pb, Zr, Ti and La. Lanthanum's incorporation seems to be effective.

5. Conclusion

The 2-stage route is an efficient way to produce homogeneous PZT powders starting from oxide precursors. These precursors must be sufficiently reactive (nanosized). As no delicate feedstock preparation is required, this method is easier than liquid based process.

The 2-stage route has not yet been optimised; the higher lead deficiency observed for those powders could easily be reduced by introducing a higher amount of precursor excess.

In comparison with our previous 1-stage process, the 2-stage route is a successful way to incorporate lanthanum in the PZT network.

A multi-stage process could therefore be developed: such a method, would be a promising way to control the dopants incorporation, especially when many dopants are used.

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