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# Phase formation of ferroelectric perovskite 0.75 Pb(Zn$_{1/3}$,Nb$_{2/3}$)O$_3$–0.25 BaTiO$_3$ prepared by aqueous solution–gel chemistry†

**Kristof Van Werde, Geert Vanhoyland, Daniël Nelis, Dirk Mondelaers, Marlies K. Van Bael, Jules Mullens* and Lucien C. Van Poucke**

*Limburgs Universitair Centrum, Laboratory of Inorganic and Physical Chemistry, IMO, B-3590 Diepenbeek, Belgium*

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Here we report on the synthesis and phase formation of perovskite 0.75 Pb(Zn$_{1/3}$,Nb$_{2/3}$)O$_3$–0.25 BaTiO$_3$ (PZN–BT) by means of a new aqueous solution–gel method. The gelation process was optimized for an ammonium PZN acetate citrate precursor. The chemical homogeneity of this precursor was investigated by means of TEM–EDX analysis (Transmission Electron Microscopy–Energy Dispersive X-ray analysis). All metal ions were found to be homogeneously dispersed in the precursor gel at least down to 10 nm. An aqueous BaTiO$_3$ precursor was synthesized and its oxide formation was investigated by means of HT-XRD (High Temperature X-ray Diffraction) and TGA–MS (Thermogravimetric Analysis on-line coupled to Mass Spectrometry). The gel-to-oxide transition of the PZN–BT precursor was studied using HT-XRD and TGA–MS. It was concluded that 96+ weight% perovskite PZN–BT could be formed out of the gel precursor if proper thermal treatment is applied (14 minutes sintering at 800 °C after fast firing at 50 °C min$^{-1}$). Finally a phase formation mechanism for perovskite PZN–BT is proposed: perovskite 0.75 Pb(Zn$_{1/3}$,Nb$_{2/3}$)O$_3$–0.25 BaTiO$_3$ is formed out of a cubic pyrochlore PZN. At 850 °C the perovskite decomposes irreversibly into that same pyrochlore together with volatile PbO and ZnO. The evolution of PbO was proved with TGA.

## 1. Introduction

In our laboratory an aqueous solution–gel technique, a so-called 'wet' or 'chemical' method, is used to synthesize several ferroelectric multicomponent metal oxides such as Pb(Zr,Ti)O$_3$, Pb(Zn$_{1/3}$,Nb$_{2/3}$)O$_3$, SrBi$_2$Ta$_2$O$_9$, (Bi$_{3.75}$,La$_{0.75}$)-Ti$_3$O$_{12}$ and BaTiO$_3$.[1,2] By realizing a chemically homogeneous and amorphous gel out of a solution, containing all metal ions bound to tailor-made organic ligands, one is able to form the desired ceramic powder through thermal decomposition of the organic matrix in the gel and subsequent oxide crystallization.[3–5] By spincoating the solution on a proper substrate, followed by subsequent gelation and thermal treatment, one is able to make thin oxide films.[6] These thin ferroelectric films can be used in electronics as non-volatile ferroelectric random access memories (NV-FeRAM)[7] and multilayer ceramic capacitors (MLCC).[8]

One of the interesting ferroelectric materials for thin film applications is Pb(Zn$_{1/3}$,Nb$_{2/3}$)O$_3$ (PZN). PZN, being a relaxor perovskite, features the desired dielectric properties for MLCC and FeRAM applications.[9] However until now, phase pure perovskite (Pe) PZN has not been synthesized under ambient pressure,[10] since perovskite formation is inhibited during thermal treatment by phase segregation of (non-ferroelectric) pyrochlore phases (Py). These pyrochlores have disastrous physical and electronic properties for the above applications.[11] In order to avoid this phase segregation, one has to understand the reaction mechanism as well as the thermodynamics behind Pe PZN phase formation.[12]

A diversity of reaction mechanisms for the formation of Pe Pb(B$_{1/3}$,Nb$_{2/3}$)O$_3$ (PBN) from mechanically mixed oxides or amorphous sol–gel precursors have been proposed in the literature (B being a doubly charged positive ion: Mg$^{2+}$, Ni$^{2+}$, Cd$^{2+}$). Lejeune *et al.*[13] stated that during thermal treatment of a ground metal oxide mixture of PbO, BO and Nb$_2$O$_5$ several pyrochlores (Pb$_3$Nb$_2$O$_{8(\mathrm{ort})}$, Pb$_2$Nb$_2$O$_{7(\mathrm{rho})}$, Pb$_3$Nb$_4$O$_{13(\mathrm{cub})}$) are formed. The first two pyrochlores react with PbO and BO at higher temperature, near the eutectic of PbO and Nb$_2$O$_5$ (~830 °C), with formation of Pe PBN as a result. These authors described the cubic pyrochlore Pb$_3$Nb$_4$O$_{13}$ to be non-reactive to BO and, as a result, this pyrochlore remains situated around the perovskite grains causing the loss of the optimal dielectric properties.[14a] Lejeune *et al.* also described PbO volatility and accompanying decomposition of Pb$_2$Nb$_2$O$_{7(\mathrm{rho})}$ into Pb$_3$Nb$_4$O$_{13(\mathrm{cub})}$. Hence, the cubic pyrochlore is formed irreversibly. On the other hand, Inada *et al.*[14b] stated Pb$_3$Nb$_4$O$_{13(\mathrm{cub})}$ is not inert with respect to perovskite formation. These authors described this cubic pyrochlore to be formed at lower temperatures (530–600 °C) and to react with PbO at 600–700 °C with formation of Pb$_2$Nb$_2$O$_{7(\mathrm{rho})}$ as a result. It is the latter that reacts at elevated temperature with BO leading to Pe PBN. Shrout *et al.*,[12] Halliyal *et al.*[15] and Goo[16] also described a similar cubic pyrochlore phase being formed at first. However, they believe Pb$_3$Nb$_4$O$_{13(\mathrm{cub})}$ is partially accessible for BO at lower temperatures. It is their opinion that Pb$_{1.83}$B$_{0.29}$Nb$_{1.71}$O$_{6.39(\mathrm{cub})}$ reacts with BO and PbO at elevated temperature (800 °C) to form Pe PBN. However, after long sintering times, Pe PBN decomposes into Pb$_3$Nb$_4$O$_{13(\mathrm{cub})}$, BO and PbO. Again it was concluded that gaseous evolution of PbO at ~800 °C leads to the irreversible formation of a cubic pyrochlore phase and BO. In order to account for this undesirable decomposition, often an excess of PbO is added to stoichiometric PbO–BO–Nb$_2$O$_5$ system.[17]

The use of an excess of PbO, proper control of the applied temperature program and optimization of sintering times have led to the realization of most of the Pe PBN oxides (Pe Pb(Mg$_{1/3}$,Nb$_{2/3}$)O$_3$, Pe Pb(Ni$_{1/3}$,Nb$_{2/3}$)O$_3$, Pe Pb(Cd$_{1/3}$,Nb$_{2/3}$)O$_3$).[18–20] However, it remained impossible to synthesize phase pure Pe Pb(Zn$_{1/3}$,Nb$_{2/3}$)O$_3$ at ambient pressure. At first it was presumed

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ZnO is insufficiently dispersed in the mixed oxide precursor prepared by mixing and grinding the constituent metal oxides (PbO, BO, $Nb_2O_5$). Such processing leads to precursors in which metal oxides are mixed on the micrometer level, inevitably giving rise to higher processing temperatures, longer sintering times and, as a result, phase segregation. Therefore, several investigators tried to synthesize precursors in which all metal ions are chemically mixed on the molecular level. However, neither by a coprecipitation method[21] nor by an alcoholic sol–gel synthesis were they able to obtain phase pure Pe PZN.[22] In both cases a cubic pyrochlore is obtained. These results made authors think about the thermodynamical stability of PZN. Shrout *et al.*[12] published two main principles for thermodynamical stability of perovskites. On the basis of the constituent cation radii (Goldschmidt tolerance) and the cation–anion interaction (electronegativity difference) these authors were able to predict the thermodynamical stability of almost all perovskite PBN systems; with the exception of PZN, however. For that reason Wakiya *et al.* performed valence bond calculations on the cubic Pe $Pb(B_{1/3},Nb_{2/3})O_3$—and cubic Py $Pb_{3.72}(B_{0.48},Nb_{3.52})O_{13}$—system.[23] They concluded that the lead–oxygen interaction was weakest in the perovskite phase, especially when the B-ion was $Zn^{2+}$. These authors also concluded that the free electron pair (inert pair) of $Pb^{2+}$ interacted repulsively with the other ions in the perovskite lattice.[24]

By these calculations Wakiya *et al.* explained why Pe $(1-x)$ $Pb(Zn_{1/3},Nb_{2/3})O_3$–$x$ $BaTiO_3$ could be synthesized: replacing the $Pb^{2+}$-ion diminishes the inert pair repulsion by $Ba^{2+}$ in the lattice. Wakiya *et al.* as well as Shrout *et al.* concluded that PZN is also difficult to form because of the tendency of $Zn^{2+}$ to be in a 4-coordinated covalent structure (*e.g.* wurtzite). Since cubic pyrochlore phases have more affinity towards covalency than the rather ionic perovskite phase, it is more likely to form $Zn^{2+}$-containing pyrochlores than perovskites. By incorporating $BaTiO_3$ in the lattice (at the lattice positions of PZN), the overall B site occupation becomes more ionic, leading to easier perovskite formation.

## 2. Experimental

### 2.1. Methods and apparatus

For HT-XRD measurements a modified Siemens D-5000 powder diffractometer with Cu-$K_\alpha$ as the radiation source was used. The configuration consisted of a Göbel mirror ($K_{\alpha 1+2}$, Huber), a high temperature device with a Pt rod (Anton Paar, HTK 10) and a position sensitive detector (Braun). The Pt rod also gave contributions to the diffraction pattern at 39.76, 46.24 and 67.45° $2\theta$. For this study the equipment was operated in the hot-stage mode. With this configuration it is possible to take *in situ* diffractograms during heating of the sample in static air. For HT-XRD measurements a heating rate of 10 °C $min^{-1}$ was considered.

TGA–MS measurements were performed with a TGA 951-2000 apparatus from TA Instruments on-line coupled to a quadrupole mass spectrometer (Model Thermolab of VG Fisons Instruments), using a flexible heated silica lined steel capillary and a molecular leak. The exact coupling is described elsewhere.[25] In order to identify the evolution of a gas, several *m*/*z* values corresponding with the gas were plotted as a function of time.[26] The carrier gas used was a dry air-like mixture of $O_2$ and $N_2$ (Air Liquide) at a flow rate of 75 mL $min^{-1}$. In all TGA–MS experiments a heating rate of 10 °C $min^{-1}$ was applied.

Metal ion concentrations in solution were determined with ICP–AES (Inductively Coupled Plasma–Atomic Emission Spectroscopy) on a Perkin-Elmer Optima 3000 DV. TEM studies were performed on a Philips CM12 at 120 kV equipped with a EDX analyzer (EDAX).

### 2.2. Materials and reagents

The following materials and reagents were used: zinc acetate dihydrate (Aldrich, 98+% $Zn(OOCCH_3)_2 \cdot 2H_2O$), citric acid (Aldrich, 99% $C(OH)(COOH)(CH_2COOH)_2$), ammonia solution (UCB, p.a. $NH_3$ *ca.* 25% in $H_2O$), niobium(V) ammonium oxalate (H.C. Starck, 20.7% in Nb), barium acetate (Aldrich, 99% $Ba(OOCCH_3)_2$), lead acetate trihydrate (Merck, p.a. $Pb(OOCCH_3)_2 \cdot 3H_2O$), titanium(IV) isopropoxide (Acros, 98+%, $Ti(OPr^i)_4$) and hydrogen peroxide (Acros Organics, p.a. 35% $H_2O_2$ solution in $H_2O$, stabilized).

### 2.3. Preparation of the precursor gel

A 0.2 mol $L^{-1}$ ammonium citrate solution was prepared by dissolution of citric acid in water and subsequent ammonia addition until pH 7. A 1 mol $L^{-1}$ $Pb(OOCCH_3)_2 \cdot xH_2O$ solution and a 1 mol $L^{-1}$ $Zn(OOCCH_3)_2 \cdot 2H_2O$ solution were prepared. A 0.2 mol $L^{-1}$ Nb(V) peroxo-citrato precursor solution was prepared by a synthesis route similar to that of Narendar *et al.*,[27] although some small adjustments were made.[28] The exact metal ion concentration of every solution was determined by ICP–AES. In order to study the influence of the amount of ligand (citric acid) and the pH on precursor homogeneity, we investigated several PZN precursor solutions, as shown in Table 1. All these solutions were prepared in the same way, as illustrated in Fig. 1.

To 12.5 mL of the 0.2 mol $L^{-1}$ ammonium citrate solution the desired amount of the $Pb^{2+}$ acetate solution was added. Addition of the stoichiometric amount of either the $Nb^{5+}$ peroxo-citrato or the $Zn^{2+}$ acetate solution followed. Finally the pH was adjusted by addition of ammonia. Table 1 shows which of the solutions remain clear after addition of all the metal ion solutions.

Narendar *et al.* described lead citrate solutions to be unstable at a pH below 8.0 and a Cit : $Pb^{2+}$ ratio below 4 : 1. Here it is found that every solution of pH 7.5 is unstable, due to $Pb_3Cit_2$ precipitation.[29] A Cit : $Pb^{2+}$ ratio of 3 : 1 is here already sufficient to avoid precipitation at higher pH (Cit : M ratio of 1.5 : 1, M being the total metal ion concentration). In order to have as few as possible organic materials in the precursor gel and in order to avoid a lot of $NH_3$ in solution, the precursor solution of pH 8.5 and Cit : M 2 : 1 will be used for gelation and thermal investigation.

The addition of the lead citrate (or zinc citrate) solution to the peroxo-citrato Nb(V) precursor solution gives rise to a change in color from pale yellow to deep golden yellow,

**Table 1** Stability of precursor solutions as a function of pH and citric acid to overall metal ion concentration

| Cit : M | pH 7.5 | pH 8.0 | pH 8.5 | pH 9.0 | pH 9.5 |
|---|---|---|---|---|---|
| 4 : 1 | Precipitation | Clear solution | Clear solution | Clear solution | Clear solution |
| 3 : 1 | Precipitation | Clear solution | Clear solution | Clear solution | Clear solution |
| 2.5 : 1 | Precipitation | Clear solution | Clear solution | Clear solution | Clear solution |
| 2 : 1 | Precipitation | Clear solution | Clear solution | Clear solution | Clear solution |
| 1.5 : 1 | Precipitation | Clear solution | Clear solution | Clear solution | Clear solution |
| 1 : 1 | Precipitation | Precipitation | Precipitation | Precipitation | Precipitation |
| 0.66 : 1 | Precipitation | Precipitation | Precipitation | Precipitation | Precipitation |

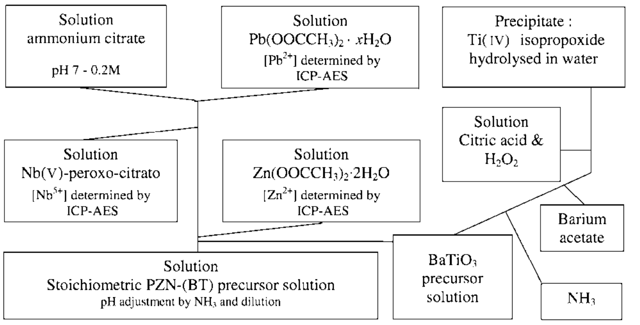

**Fig. 1** Aqueous solution–gel synthesis of PZN–BT

indicating a reaction between the citrato $Pb^{2+}$ (or citrato $Zn^{2+}$) precursor species and the peroxo-citrato Nb(v) complex. As shown in luminescence spectroscopy for the peroxo-citrato PMN precursor by Narendar *et al.*,[30] heterometallic species containing all three cations are formed. Through the deprotonated hydroxyl group of the citrate ligand oxygen bridges are formed between the different metal ions within the heteropolynuclear complex.[27,30]

This precursor solution was poured into a Petri vessel and the solvent was evaporated in an oven under dry air at 65 °C. Gelation is not only caused by the increase of concentration and its resulting high viscosity: amorphous metal carboxylate gels are synthesized by crosslinking carboxylato–metal complexes into a three-dimensional gel structure. Several types of intermolecular crosslinks, such as intermolecular metal–carboxylate bonds, hydrogen bonds and ammonium–carboxylate bonds are present.[29] The intermolecular ammonium–carboxylate bond is of great importance, since a change of base (*e.g.* tetramethylammonium hydroxide instead of ammonia) does not lead to gelation. The three-dimensional network of carboxylate complexes and ammonium ions, wherein the $NH_4^+$ ion serves as the bridging crosslink, is crucial for gel formation.[27,29] Here, the resulting gel was dry, slightly yellow, transparent, homogeneous and amorphous, as could be seen in XRD.

In a similar way a new $BaTiO_3$ precursor gel was prepared, see Fig. 1. Therefore $Ti^{4+}$ isopropoxide was hydrolyzed by mixing into water. The hydrolyzed precipitate was then dissolved by addition of an aqueous solution of citric acid and $H_2O_2$. Hydrogen peroxide and citric acid were both used in a 2 : 1 ratio to $Ti^{4+}$. Then a stoichiometric amount of $Ba^{2+}$ acetate was added and the acidity was decreased until pH 8.5. This precursor solution was also poured out into a Petri vessel and the solvent was evaporated in the same way as for PZN. The resulting gel was orange, transparent, homogeneous and amorphous.

In order to obtain the $(1-x)\ Pb(Zn_{1/3},Nb_{2/3})O_3–x\ BaTiO_3$ precursor both previous precursor solutions were mixed in the desired ratio, as shown in Fig. 1.

## 3. Results and discussion

### 3.1. Phase formation of cubic pyrochlore PZN

Chemical homogeneity (a high degree of dispersion of the constituent metal ions) in the precursor gel is one of the key features in avoiding phase segregation during thermal decomposition and oxide crystallization. Any phase segregation should be avoided. Therefore some TEM investigations were performed on three freestanding PZN precursor films synthesized in different ways. Fig. 2a, b and c show PZN precursor gel films that were heated to 280 °C. These films were prepared by dotting a droplet of the precursor solution on a copper TEM grid and subsequently heating it in a TGA furnace. Fig. 2b shows the film prepared starting from the solution with a Cit : M ratio of 2 : 1 and a pH of 8.5. Fig. 2a and Fig. 2c show a

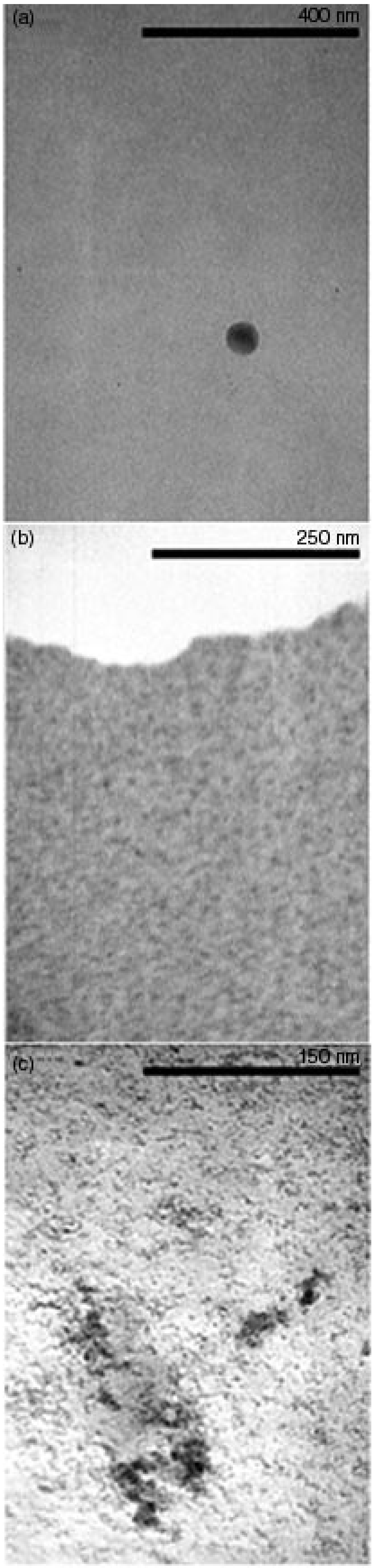

**Fig. 2** (a) TEM picture of freestanding PZN film, synthesized from a precursor solution with pH 6 and Cit : M 2 : 1. (b) TEM picture of freestanding PZN film, synthesized from a precursor solution with pH 8.5 and Cit : M 2 : 1. (c) TEM picture of freestanding PZN film, synthesized from a precursor solution with pH 10 and Cit : M 2 : 1.

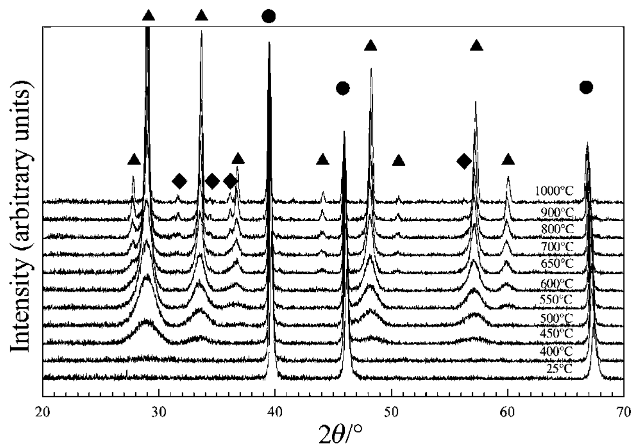

**Fig. 3** HT-XRD spectra of the stoichiometric PZN precursor (10 °C $min^{-1}$). Cubic pyrochlore Py ▲; ZnO ◆; Pt ●.

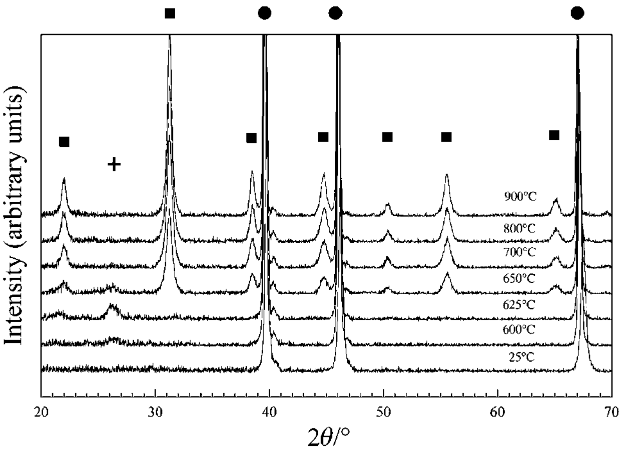

**Fig. 4** HT-XRD spectra of the stoichiometric $BaTiO_3$ precursor (10 °C $min^{-1}$). $BaTiO_3$ ■; $BaCO_3$ +.

film prepared in the same way, but starting respectively from a solution with pH 6 and pH 10. From these figures it is clear that the acidity of the precursor solution plays a significant role in the phase segregation mechanism. By means of EDX analysis it is shown that the phase segregation in Fig. 2a is due to a lead containing compound. As mentioned before $Pb_3Cit_2$ is hardly soluble at a pH below 8.0 and this could be the cause of the increased lead concentration. In Fig. 2c EDX analysis proved the precipitate contains substantially more $Zn^{2+}$. Here we presume $Zn(OH)_2$ was formed at pH 10, which is at the origin of the segregation. In Fig. 2b no chemical inhomogeneities are observed, a high degree of metal ion mixing is guaranteed down to at least 10 nm.

The HT-XRD spectra of the chemically homogeneous PZN precursor gel are shown in Fig. 3. Here it is shown that the precursor gel is amorphous at room temperature. However, the chemical homogeneity and the amorphicity can not avoid the formation of a cubic pyrochlore phase at 450 °C. The diffraction pattern resembles strongly that of $Pb_{1.83}(Zn_{0.29},Nb_{1.71})O_{6.39}$ (which has a high quality spectrum in the JCPDS database).[31] The cubic pyrochlore phase remains present during the entire thermal treatment. No perovskite PZN is formed. At elevated temperatures (700–1000 °C) zincite (ZnO) Bragg reflections are observed, indicating that $Zn^{2+}$ ions have segregated (Fig. 3). This corresponds with the formation of a cubic Py phase, like $Pb_{1.83}(Zn_{0.29},Nb_{1.71})O_{6.39}$ which is deficient in $Zn^{2+}$ (and $Pb^{2+}$) in respect to the stoichiometric perovskite precursor.

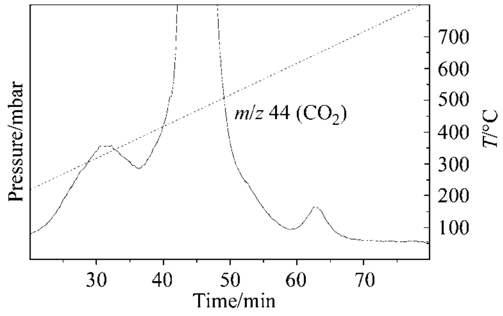

**Fig. 5** TGA–MS evolution of *m/z* 44 ($CO_2$).

### 3.2. Phase formation of Pe $BaTiO_3$ from the aqueous $BaTiO_3$ precursor

In Fig. 4 the HT-XRD spectra of the new $BaTiO_3$ precursor gel are shown. One can observe the Pe $BaTiO_3$ formation from an amorphous precursor at 650 °C. However, the diffractograms at 600 and 625 °C show a broad, unknown Bragg reflection at 26° 2*θ*. This reflection might be caused by $BaCO_3$, however it could not be assigned with great certainty using the JCPDS database.

To prove this reflection is due to $BaCO_3$, a TGA–MS experiment was performed. Fig. 5 shows the evolution of *m/z* 44 ($CO_2$) as a function of time during thermal decomposition of the gel. After 60 minutes (~640 °C) a final substantial evolution of $CO_2$ is observed, clearly indicating the decomposition of $BaCO_3$. It is only after decomposition of this carbonate that the Pe $BaTiO_3$ is formed (650 °C) (pure $BaCO_3$ is thermally very stable, it only decomposes at elevated temperatures. Here the ability to form $BaTiO_3$ lowers the decomposition temperature).

### 3.3. Phase formation of Pe 0.75 $Pb(Zn_{1/3}Nb_{2/3})O_3$–0.25 $BaTiO_3$ from the aqueous solution–gel precursor

Fig. 6 shows the HT-XRD spectra of the 0.75 $Pb(Zn_{1/3}Nb_{2/3})O_3$–0.25 $BaTiO_3$ precursor gel for a heating rate of 10 °C $min^{-1}$ in dry air. Again at room temperature the gel is amorphous. Initially, at 500 °C some broad cubic Py reflections are observed. However, at 575 °C they are accompanied by a set of new diffraction peaks. These reflections are all due to diffraction of the Pe 0.75 $Pb(Zn_{1/3}Nb_{2/3})O_3$–0.25 $BaTiO_3$ phase. The intensity of the perovskite peaks increases, while the Bragg reflections of the pyrochlore continue to weaken (until 800 °C). These results indicate that the perovskite phase

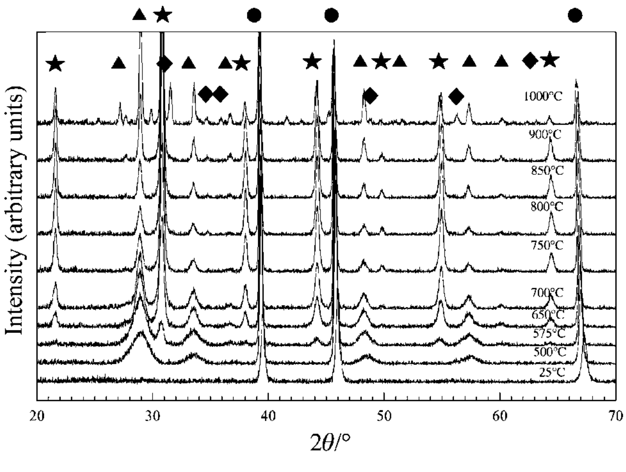

**Fig. 6** HT-XRD of the stoichiometric 0.75 PZN–0.25 BT precursor. Py Cubic pyrochlore ▲; ZnO ◆; Pt ●; Pe 0.75 PZN–0.25 BT ★.

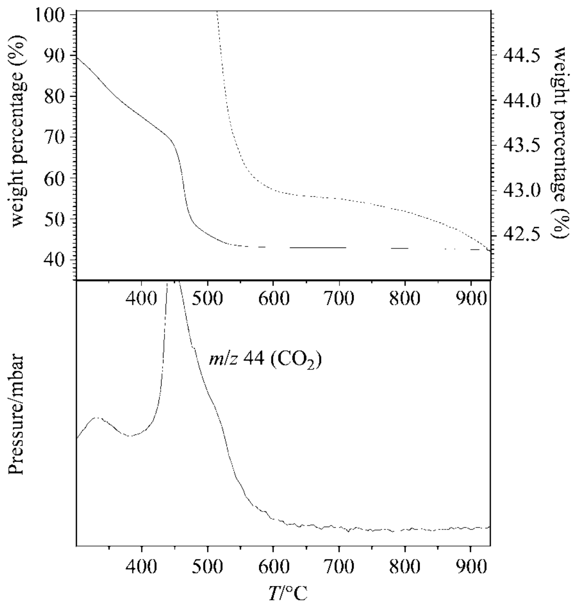

**Fig. 7** TGA–MS: Upper: weight loss as a function of temperature (full line), weight loss enlarged (dashed line). Lower: evolution of *m*/*z* 44 ($CO_2$).

is formed out of the pyrochlore phase, using the $Ba^{2+}$ ions to stabilize its lattice, as was calculated by Wakiya *et al.*[23,24]

Here, it is concluded that $Ba^{2+}$ ions are directly incorporated in the perovskite structure, since no Bragg reflections of $BaCO_3$ are observed in the HT-XRD patterns (Fig. 6). Moreover, a TGA–MS experiment performed on the PZN–BT precursor (Fig. 7) shows there is no $CO_2$ evolution caused by the decomposition of $BaCO_3$ at 640 °C. Therefore, it seems reasonable to assume no $BaCO_3$ has segregated during thermal decomposition of the precursor and the $Ba^{2+}$ ions are directly incorporated in the perovskite lattice.

The amount of pyrochlore and perovskite phases as a function of temperature can be determined from the relative intensities of the (222) pyrochlore and the (110) perovskite peak in the XRD patterns:[32,33]

$$w\%_{\mathrm{Pe}} = \frac{I_{(110)\mathrm{Pe}}}{I_{(110)\mathrm{Pe}} + I_{(222)\mathrm{Py}}}$$

Fig. 8 shows the amount of perovskite (in weight%) for a heating rate of 10 °C min$^{-1}$ in dry air. For this heating rate, a maximum of 89% conversion of Py into Pe could be obtained at 800 °C.

Above this temperature the amount of perovskite decreases again, resulting in the formation of the cubic pyrochlore (Fig. 6). This is also indicated by the formation of ZnO in HT-XRD (as was also the case for the pure PZN precursor). The TGA (Fig. 7) features a 0.15% weight loss between 700 and 800 °C, indicating the evolution of volatile PbO. At higher temperatures this weight loss becomes even more pronounced (0.7%). Therefore we conclude that heating above 850 °C inevitably leads to the decomposition of the perovskite into the cubic pyrochlore, ZnO and volatile PbO. Heating above 800°C should therefore be avoided.

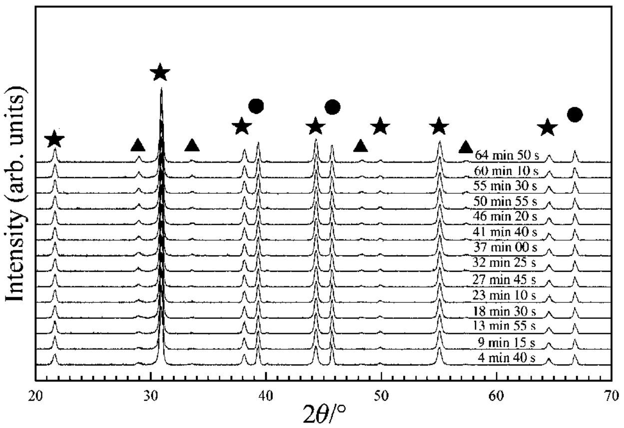

**Fig. 9** Isothermal HT-XRD spectra of the 0.75 PZN–0.25 BT precursor at 800 °C. The precursor was heated at a rate of 50 °C min$^{-1}$ in dry air. Py Cubic pyrochlore ▲; ZnO ◆; Pt ●; Pe 0.75 PZN–0.25 BT ★.

It is known that by faster heating or rapid thermal processing the formation of the perovskite phase in lead based perovskites can be improved.[34,35] At such heating rates formation of the pyrochlore phase can be avoided at lower temperatures, leading to direct formation of the perovskite phase. Therefore the precursor sample was heated to 800 °C at a heating rate of 50 °C min$^{-1}$ in dry air, whereafter it was isothermally treated (the precursor was not heated above 800 °C, for the above reason of PbO evaporation). Fig. 9 shows the isothermal XRD patterns.

Directly after ramping a conversion of 94% was obtained, as shown in Fig. 10. Moreover, after isothermal sintering for 14 minutes the weight percentage of perovskite became over 96%. This is a remarkable gain of perovskite phase, since a rather moderate heating rate was used (50 °C min$^{-1}$ is low as compared to rapid thermal processing).

After this period of time, the amount of perovskite decreases again. The probable cause of this change is PbO evaporation out of the perovskite lattice, leading to the cubic pyrochlore and ZnO. After one hour of sintering only 91% of perovskite remains (Fig. 10).

The improving effect of the heating rate indicates the importance of proper thermal treatment in perovskite formation. For the synthesis of this compound further investigations

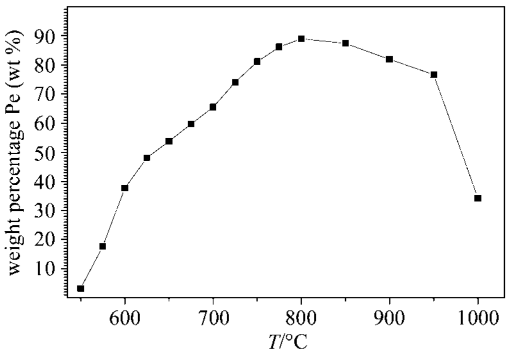

**Fig. 8** Weight percentage perovskite phase as a function of temperature for the 0.75 PZN–0.25 BT precursor heated up at 10 °C min$^{-1}$ in dry air.

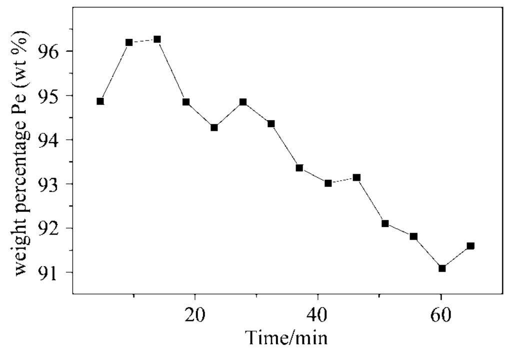

**Fig. 10** Weight percentage perovskite phase as a function of time at 800 °C. The 0.75 PZN–0.25 BT precursor was heated to 800 °C at 50 °C min$^{-1}$ in dry air.

need to be made in order to obtain 100% phase pure PZN–BT. The above experiment indicates rapid thermal annealing might be a proper solution.

## 4. Conclusion

A new, aqueous solution–gel method was applied for the synthesis of a $Pb(Zn_{1/3},Nb_{2/3})O_3$ precursor, a $BaTiO_3$ precursor and a 0.75 $Pb(Zn_{1/3},Nb_{2/3})O_3$–0.25 $BaTiO_3$ precursor. The first was found to be amorphous and chemically homogeneous up to 10 nm. However, no phase pure $Pb(Zn_{1/3},Nb_{2/3})O_3$ could be formed from this precursor. Instead a cubic pyrochlore is formed and ZnO segregates. By adding 0.25 $BaTiO_3$, it is possible to form 0.75 $Pb(Zn_{1/3},Nb_{2/3})O_3$–0.25 $BaTiO_3$, which has the desired perovskite structure. The perovskite is formed from the pyrochlore.

At elevated temperature, the perovskite decomposes into ZnO, volatile PbO and the cubic pyrochlore phase. The volatility of PbO above 700 °C could be derived from a 0.7% weight loss in TGA. These results state phase pure PZN is indeed a thermodynamic unstable compound, as described by Shrout *et al.*[12]

In PZN–BT it seems reasonable to assume $BaTiO_3$ not only plays a role as perovskite seeding, but also stabilizes the perovskite lattice by diminishing the inert pair repulsion effect.[23,24]

When heating at faster heating rate (50 °C $min^{-1}$), a conversion of Py in to Pe of 96+% could be obtained at 800 °C. The above experiments not only show the importance of the stabilizing $Ba^{2+}$ ion, but also the improving effect of proper thermal treatment. It is thereby concluded that the thermal treatment needs further investigation.

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## References

1 R. Nouwen, J. Mullens, D. Franco, J. Yperman and L. C. Van Poucke, *Vibrat. Spectrosc.*, 1996, **10**, 291.
2 J. Mullens, K. Van Werde, G. Vanhoyland, R. Nouwen, M. K. Van Bael and L. C. Van Poucke, *Proc. 28th NATAS conference (North American Thermal Analysis Society), Orlando, USA*, ed. K. J. Kociba, Omnipress, Madison, WI, 2000, p. 95.
3 M. K. Van Bael, E. Knaepen, A. Kareiva, I. Schildermans, R. Nouwen, J. D'Haen, M. D'Olieslaeger, C. Quaeyhaegens, D. Franco, J. Yperman, J. Mullens and L. C. Van Poucke, *Supercond. Sci. Technol.*, 1998, **11**, 82.
4 M. K. Van Bael, A. Kareiva, R. Nouwen, I. Schildermans, G. Vanhoyland, J. D'Haen, M. D'Olieslaeger, D. Franco, J. Yperman, J. Mullens and L. C. Van Poucke, *Int. J. Inorg. Mater.*, 1999, **1**, 259.
5 J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.*, 1988, **18**, 259.
6 D. J. Wouters, R. Nouwen, G. J. Norga, A. Bartic, L. C. Van Poucke and H. E. Maes, *J. Phys. IV France*, 1998, **8**, 205.
7 O. Auciello, J. F. Scott and R. Ramesh, *Physics Today*, 1998, 22.
8 Y. Yamashita, *Am. Ceram. Soc. Bull.*, 1994, **73**, 74.
9 M. L. Mulvihill, L. E. Cross and K. Uchino, *J. Am. Ceram. Soc.*, 1995, **78**, 3345.
10 Y. Matsuo, *J. Am.Ceram. Soc.*, 1969, **52**, 516.
11 S. Y. Chen, C. M. Wang and S. Y. Cheng, *Mater. Chem. Phys.*, 1998, **52**, 207.
12 T. R. Shrout and A. Halliyal, *Am. Ceram. Soc. Bull.*, 1987, **66**, 704.
13 M. Lejeune and J. P. Boilot, *Ceram. Int.*, 1982, **8**, 99.
14 (*a*) G. Desgardin, H. Bali and B. Raveau, *Mater. Chem. Phys.*, 1983, **8**, 469; (*b*) M. Inada, *Jpn. Natl. Tech. Rep.*, 1977, **27**, 95.
15 A. Halliyal, M. M. A. Sekar and K. C. Patil, *J. Mater. Res.*, 1996, **11**, 1210.
16 E. Goo, *J. Am. Ceram. Soc.*, 1986, **69**, C-188.
17 J. P. Guha, D. J. Hong and H. U. Anderson, *J. Am. Ceram. Soc.*, 1988, **71**, C-152.
18 C. D. E. Lakeman and D. A. Payne, *Mater. Chem. Phys.*, 1994, **38**, 305.
19 B. Balzer and H. Langbein, *Cryst. Res. Technol.*, 1997, **32**, 955.
20 T. Ogawa, M. Ono and M. Fijiwara, *Jpn. J. Appl. Phys.*, 1995, **34**, 5306.
21 Y. Yoshikawa, *J. Eur. Ceram. Soc.*, 1999, **19**, 1037.
22 Y. Hu, *J. Mater. Sci.*, 1996, **31**, 4255.
23 N. Wakiya, K. Shinozaki and N. Mizutani, *J. Am. Ceram. Soc.*, 1997, **80**, 3217.
24 N. Wakiya, N. Ishizawa, K. Shinozaki and M. Mizotani, *Mater. Res. Bull.*, 1995, **30**, 1121.
25 J. Mullens, in *Handbook of Thermal Analysis and Calorimetry*, vol. 1., ed. M. Brown and P. Gallagher, Elsevier, Amsterdam, 1998, p. 509.
26 R. Carleer, G. Reggers, M. Ruysen and J. Mullens, *Thermochimica*, 1998, **323**, 82.
27 Y. Narendar and G. L. Messing, *Chem. Mater.*, 1997, **9**, 580.
28 K. Van Werde, D. Nelis, D. Mondelaers, G. Vanhoyland, M. K. Van Bael, J. Mullens and L. C. Van Poucke, to be published.
29 Y. Narendar and G. L. Messing, *Catal. Today*, 1997, **35**, 247.
30 Y. Narendar and G. L. Messing, *J. Mater. Res.*, 1999, **14**, 3921.
31 JCPDS International Centre for Diffraction Data, 1997 [Ref.: 34-0374: Pfoertsch *et al.*].
32 S. L. Swartz and T. R. Shrout, *Mater. Res. Bull.*, 1982, **17**, 1245.
33 X. Wang and B. Huang, *Ferroelectrics*, 1994, **154**, 301.
34 E. M. Griswold, L. Weaver, M. Sayer and I. D. Calder, *J. Mater. Res.*, 1995, **10**, 3149.
35 D. Saha, A. Sen and H. S. Maiti, *J. Mater. Res.*, 1996, **11**, 932.