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Characterization of $PbZrO_3$ prepared using an alkoxide-based sol–gel synthesis route with different hydrolysis conditions

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Abstract

$PbZrO_3$ precursor powders were prepared from lead acetate and zirconium *n*-butoxide in *n*-butanol and hydrolysed with R_w (molar ratio of water/lead acetate) = 2 and 15 at different pH values. Upon heating the organic groups were removed in two steps for the precursor prepared at $R_w = 2$, and in one step at $R_w = 15$. The perovskite phase crystallizes at approximately 700 °C, irrespective of the hydrolysis conditions.

Keywords: Sol–gel processes; Electron microscopy; X-ray methods; PZT

1. Introduction

Sol–gel processing can be used to produce powders, fibres, thin films and monoliths with a controlled compositions and microstructures. The structure, properties, and performance of the final ceramic material are strongly connected to the stoichiometry, homogeneity and purity of the starting precursors.[1]

The alkoxide-based sol–gel route has been used for the synthesis of $Pb(Zr,Ti)O_3$ (PZT).[2] The morphology of the $Pb(Zr_{0.5}Ti_{0.5})O_3$ powder depends on the precursors: gel fragments or soft agglomerates are obtained when propoxide or *n*-butoxide derived precursors are used, respectively.[3] Different catalysts lead to different physical characteristics of the $PbTiO_3$ produced using the 2-methoxyethanol route: acid-catalysed gels have a fibrous morphology with a homogenous distribution of constituent metals, while the base-catalysed gels have a highly condensed structure, with a coarse texture and an inhomogeneous cation distribution.[4]

In this paper $PbZrO_3$ (PZ) is studied as the end member of the PZT solid solution. PZ precursors, synthesized from lead acetate and zirconium butoxide in butanol, were hydrolysed with different amounts of water and at different values of pH. The impact of the hydrolysis conditions on the decomposition pathway, the homogeneity and the morphology of the powders are assessed.

2. Experimental procedure

The starting reagents were dehydrated lead acetate ($Pb(OOCCH_3)_2$), zirconium *n*-butoxide *n*-butanol complex ($Zr[O(CH_2)_3CH_3]_4CH_3(CH_2)_3OH$), Alfa Aesar, and 1-butanol ($CH_3(CH_2)_3OH$) Aldrich, 99.9%, as a solvent. The metal content of the starting compounds was determined gravimetrically.

Ten millimoles of lead acetate are dissolved in 10 millimoles of zirconium butoxide and 90 ml of *n*-butanol at ~70 °C, refluxed for 1 h with constant stirring followed by distillation to remove the volatile by-products.

The 0.2 M sol was cooled to 0 °C and hydrolyzed as follows: in a neutral medium with a mixture of distilled water/*n*-butanol, in alkaline medium with ammonia (25%, GR, Merck)/*n*-butanol and in an acidic medium with nitric acid (65%, GR, Merck)/water/*n*-butanol.

In the neutral medium (pH ≈ 6) the molar ratios of water/Pb-acetate (R_w) were 2 and 15 and so the precursors were denoted as PZ2 and PZ15, respectively. The precursors, hydrolysed in the alkaline medium (pH = 11) with $R_w = 15$ and in the acidic medium (pH = 3) with $R_w = 2$ were denoted as 11PZ15 and 3PZ2, respectively.

During the hydrolysis with $R_w = 2$ and pH = 6, a stiff translucent gel developed in about 5 min, while at pH = 3 an opaque gel formed. For $R_w = 15$ a semisolid milky-translucent gel

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was obtained at pH = 6, while at pH = 11 a white suspension formed.

In all cases the hydrolysis products were dried at 150 °C/12 h, and then crushed in an agate mortar with a pestle. Selected powders were heated to 700 °C/1 h.

The thermal behaviour of the dried powders was investigated from room temperature to 640 °C using thermogravimetric analysis (TG) and differential thermal analysis (DTA) (Netzsch STA 409) coupled with a mass spectrometer (Thermostar GSD300T Balzers) for the evolved-gas analysis (EGA). The experiments were conducted in flowing air, using a Pt crucible, with a heating rate of 10 °C/min. The phase composition of the powders was investigated using X-ray diffraction (Bruker AXS D4 Endeavor diffractometer, Cu Kα). The morphology of the powders was analysed using scanning electron microscopes: a SEM JEOL JSM 5800 and a Zeiss SUPRA 35VP. The median particle size (d_{50}) was measured with a laser granulometer (Cilas Alcatel) in isopropanol and the specific surface area (SSA) was measured with a BET (Micrometrics Gemini).

3. Results and discussion

The dried powders, hydrolysed in neutral and alkaline media, were amorphous, wheareas the XRD pattern of the sample hydrolysed at pH = 3 contained the main reflections of lead nitrate (XRD patterns not shown here). This means, that the oxygen bridge, which is supposed to form between the Pb and Zr atoms[5] during the synthesis of the precursor, is not strong enough or can be easily destroyed by adding nitric acid, leaving the lead segregates as lead nitrate. For this reason, the characterization of PZ will focus only on the powders prepared in the neutral and alkaline media.

The thermal behaviours of PZ2, PZ15 and 11PZ15 were investigated using the TG/DTA/EGA (Fig. 1). The PZ2 decomposed in three steps, while the PZ15 and the 11PZ15 decomposed in only two steps; the total mass losses were about 16%.

The mass losses and gases evolved in different temperature ranges are summarized in Table 1. Physically absorbed water was evolved between 25 and 220 °C. Between 220 and 400 °C, the decomposition of the acetate and alkoxide groups occurred as confirmed by the evolution of H_2O, CO_2 and acetone, while between 400 and 640 °C, CO_2 was evolved but only for the PZ2 sample.

The organic groups were removed in one step for the PZ15 and 11PZ15, and in two steps for the PZ2, which also exhibits the largest mass loss associated with the decomposition of the organics. A similar, two-step decomposition of the organic groups was reported by Malic et.al.[6] for the propoxide-derived PZ precursor ($R_w = 10$).

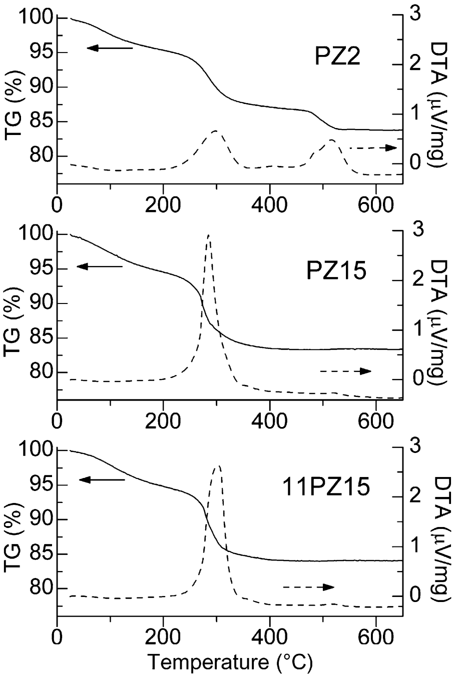

Fig. 1. TG–DTA curves of PZ2, PZ15 and 11PZ15.

To gain further insight into the processes occurring during the organic groups' decomposition, the three samples were quenched at 460 °C: the PZ2 powder was black, while the PZ15 and 11PZ15 powders were light yellow. The XRD patterns of the quenched powders exhibit reflections of metallic lead in the amorphous matrix in PZ2, while for PZ15 and 11PZ15 they were amorphous (Fig. 2).

Polli et.al.[7] observed the segregation of lead upon heating the PZT (50/50) precursor prepared from lead acetate, zirconium butoxide, titanium propoxide in ethanol, and they avoided it only by a pyrolysis step at 300 °C/1 h.

After heating at 500 °C all the PZ powders crystallized into a pyrochlore-type phase, and at 700 °C they always formed the perovskite phase with some traces of pyrochlore, irrespective of the hydrolysis conditions (Fig. 2).

Table 2 presents the SSA of the PZ powders, heated at 700 °C. For the PZ2 powder, it is very low, about 0.01 m^2/g; for the PZ15 and 11PZ15 powders it is about 1000 times higher.

Table 1
Mass losses and gases evolution of PZ precursors determined by TG/EGA in different temperature ranges

Sample	*T*-range						
	25–220 °C		220–400 °C		400–640 °C		25–640 °C
	TG (%)	EGA	TG (%)	EGA	TG (%)	EGA	TG (%)
PZ2	4.99	H_2O	8.41	H_2O, CH_3COCH_3, CO_2	2.78	CO_2	16.18
PZ15	5.88	H_2O	10.71	H_2O, CH_3COCH_3, CO_2	–	–	16.59
11PZ15	5.59	H_2O	10.31	H_2O, CH_3COCH_3, CO_2	–	–	15.89

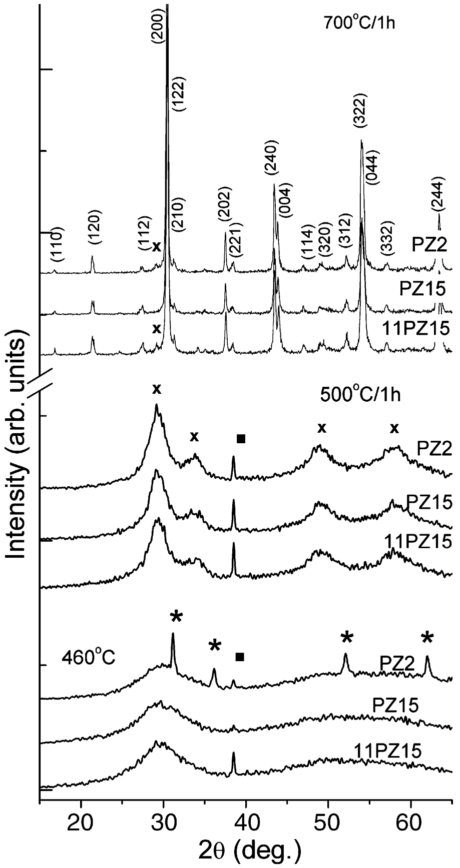

Fig. 2. XRD patterns of PZ powders after different heat treatment. The main reflections of the perovskite phase are marked; (■) sample holder, (*) metallic lead, (X) pyrochlore type phase.

Table 2
SSA of PZ powders after heat treatment at 700 °C/1 h

Sample	PZ2	PZ15	11PZ15
SSA (m^2/g)	0.011	8.463	12.832

The PZ2 and PZ15 powders heated at 700 °C were comprised of coarse fragments as revealed by SEM pictures (Fig. 3). At a higher magnification it is clear, that the fragments are more densely packed in the case of the PZ2 than the PZ15, and this agrees well with the very low SSA obtained for the PZ2 and the much higher value obtained for the PZ15. The calculated particle size, d_{BET}, for the PZ15 powders was determined to be 88 nm. The 11PZ15 powder consisted of agglomerates of fine particles; its specific surface area was 12.8 m^2/g which corresponds to a particle size of 58 nm, while the d_{50} determined by laser granulometry was 7.28 μm. The strong agglomeration of the particles was reflected in an agglomeration factor $F_{\mathrm{ag}} = 125$.

It has been reported for transition-metal (TM) alkoxides that monolithic gels form at low R_{w} and at low pH, while particulate gels or precipitates form at high R_{w} and at high pH.[8] In our case we relate the different microstructures of the powders to the different pathways of condensation induced by changes in R_{w} and pH.

We assume that like in the case of TM alkoxides, in the PZ precursor hydrolysed with $R_{\mathrm{w}} = 2$ the translucent gel, formed during hydrolysis, is composed of polymer chains that yield dense gel fragments upon further heating, while at $R_{\mathrm{w}} = 15$ and in neutral or alkaline media the semi-solid gel or precipitate is composed of cross-linked polymers which yield a powder with a porous microstructure after heating.

When heating the PZ2 precursor, its dense microstructure hinders the access of air to the interior of the gel fragments. As a consequence the organic groups not only oxidize but they also suffer a thermal decomposition to carbonaceous residues, which are then oxidized to produce CO_2 only upon further heating in the second step of the organic decomposition (Fig. 1, Table 1). The locally formed reducing atmosphere causes a partial reduction of Pb^{2+} to metallic lead (Fig. 2). Polli et. al.[7] and Coffman et.

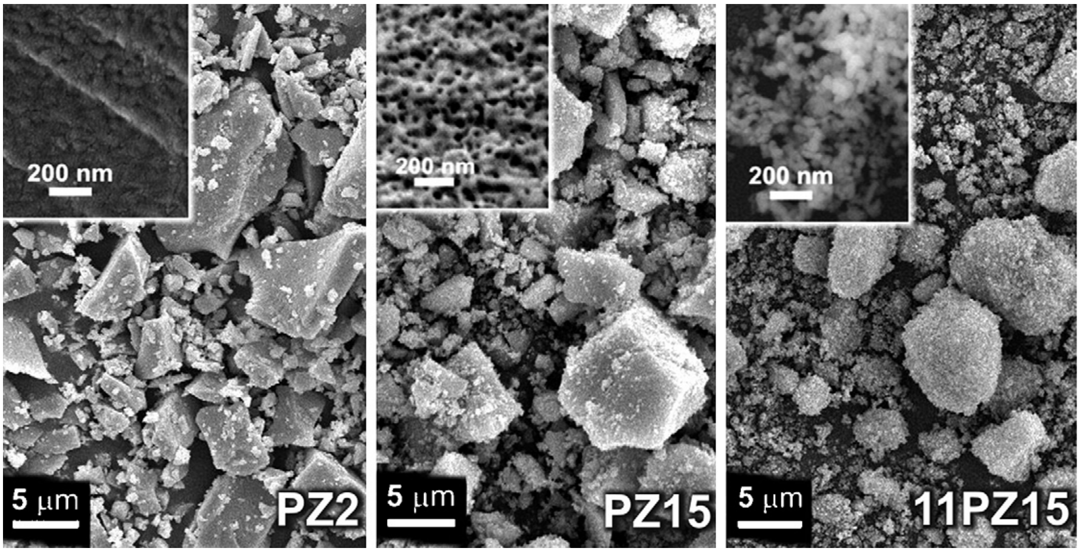

Fig. 3. SEM micrographs of PZ powders heated at 700 °C/1 h.

al.[9] also report the presence of metallic lead in the process of the thermal decomposition of PZT precursors and they also relate this to the presence of carbonanceus residues that provide a low oxygen partial pressure during heating.

The porous microstructure of the PZ precursors hydrolysed at $R_w = 15$ facilitates the access of air and the oxidation of organic groups in one step, as confirmed by the thermal analysis (Fig. 1). We concluded that in this case the partial pressure of oxygen is high enough to avoid the partial reduction of Pb^{2+} as in the case of PZ2 (Fig. 2).

4. Conclusions

$PbZrO_3$ was prepared from lead acetate, zirconium butoxide and butanol as a solvent. The hydrolysis was performed in acidic, neutral and basic media with different amounts of water. Lead nitrate was observed to segregate from the amorphous matrix if the hydrolysis is performed at pH = 3.

Upon heating, the organic groups were removed in two steps for the precursor prepared at $R_w = 2$, and in one step at $R_w = 15$. In the precursors, prepared at $R_w = 2$, the organics decomposed with intermediate carbonaceous residues forming a locally reducing atmosphere, and as a consequence metallic lead was found to segregate. A porous structure of the precursors prepared at $R_w = 15$ facilitated the oxidation of organic groups and in this case the homogeneity was retained. After heating at 700 °C the powder crystallized with the perovskite structure for all hydrolysis conditions. Agglomerated particles with a size of about 60 nm were obtained when the hydrolysis was performed at $R_w = 15$ in an alkaline medium.

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