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Influence of hydrolysis conditions of the acetate sol–gel process on the stoichiometry of PZT powders

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Abstract

$[Pb(Zr,Ti)(OAc)_x(OR)_y]$ acetate-alkoxide precursor was prepared by chelating from organic Pb, Zr and Ti alkoxides by their dissolution in various amounts of acetic acid (AcOH). Sols were formed by hydrolysis of acetate-alkoxides with ethylene glycol and transformed by polycondensation to a gel at 80 °C. The final stoichiometry of prepared PZT gels was determined by chemical analysis after their filtration and calcination at 500 °C. As results from the DTA/TGA, IR and XRD analysis, the optimum mole ratio of (Pb + Zr + Ti) to AcOH for preparation of viscous polycondensed stoichiometric gel is 1:7 and a pure perovskite phase is formed at 500 °C. The stoichiometric ratio in PZT calcinate was degraded after increasing the added amount of AcOH. At a low AcOH concentration, two-phase (pyrochlore and perovskite) regions are formed during gellation. At 700 °C, the decomposition of a pyrochlore phase and the formation of a perovskite phase takes place despite significant cation nonstoichiometry in PZT powders.

Keywords: A. Sol–gel processes; Lead titanyl zirconyl acetate precursor; Polycondensation; PZT powders; $Pb(Zr_{0.53}Ti_{0.47})O_3$

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1. Introduction

The sol–gel process allows the synthesis of ceramics materials of high purity and homogeneity by means of preparation techniques different from the traditional process of or solid state reaction of oxides [1,2]. This process occurs in a liquid solution of metallorganic precursors, which, by means of hydrolysis and condensation, lead to the formation of a new phase—a sol, and condense in a gel. Polymeric gels involve the creation of a three dimensional network when the precursors used undergo hydrolysis-polycondensation reactions and are used to make monoliths, fibers, powders and thin films.

The most common choice of precursors when making sol–gel are metal alkoxides $[M(OR)_x]$. The reaction can be described as a hydrolysis of the precursor, leading to the formation of M–OH bonds, followed by a polycondensation process with the departure of a water molecule or an alcohol molecule [3,4]. In general, the course of the sol–gel process can be described using the following equations:

$$M(OR)_x + mH_2O \rightarrow M(OR)_{x-m}(OH)_m + mROH \quad \text{hydrolysis} \tag{1}$$

$$2M(OR)_{x-m}(OH)_m \rightarrow (RO)_{x-m}(OH)_{m-1}\text{M-O-M}(OR)_{x-m}(OH)_{m-1} + H_2O \quad \text{water condensation} \tag{2}$$

$$2M(OR)_{x\text{-}m}(OH)m \rightarrow (RO)_{x-m}(OH)_{m-1}\text{M-O-M}(OR)_{x-m-1}(OH)_m + ROH \quad \text{alcohol condensation} \tag{3}$$

The polymeric precursor method was originally developed by Pechini and it is based on the chelation of a metallic cation by a carboxylic acid, such as citric, or acetic acid, and the further polymerization promoted by the addition of ethylene glycol and the consequent polyesterification [6]. The formed gels are characterized by the concentration of ions and viscosity. The conversion

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of an organic gel into inorganic oxides takes place in the following steps: drying and pyrolysis of organics, structural rearrangement, densification and crystallization [4]. The calcination temperature and the pyrolysis conditions influence the formation of the resulting perovskite phase. Besides the desired perovskite phase, a metastable fluorite phase can also be formed [5]. Ceramic powders prepared via sol-gel methods are advantageous namely from the viewpoint of sintering process for their small particle sizes (tens of nanometers).

To produce ferroelectric lead zirconate titanate [$Pb(Zr_xTi_{1-x})O_3$] composition, lead acetate $Pb(OAc)_2.3H_2O$, $Zr(OR)_x$ and $Ti(OR)_x$ alkoxides, which react with alcohol (2-methoxyethanol; 1,3 propanediol) or acetic acid (AcOH) [6–8], in a variety of sol–gel processes (where Ac is the acetate group CH_3CO–) have been used. Acetylacetone is also used as a stabilizer for alkoxides [9]. By mixing Pb, Zr and Ti precursors, a heterometallic alkoxide solution is formed and by adding a hydrolyzing agent a sol is formed, which passes through further polycondensation to form a PZT gel. Acidic or basic hydrolyzing agents influence the pore structure and stoichiometry of the gel. In the acetate-alkoxide sol–gel method of synthesis, the quantities of the AcOH solvent, as well as of the used agent (ethylene glycol and H_2O, or NH_3) have an effect on the overall stoichiometry, homogeneity and particle size of a PZT gel. According to references, the molar ratio of (Pb + Zr + Ti):AcOH = 1:10 and the hydrolyzing factor (in case of H_2O as a hydrolysing agent) $h = 0.87$ are the optimum parameters [8,6], where h is the mole ratio of the used hydrolyzing agent to the PZT phase (h = [agent]/ [PZT]).

The hydrolysis conditions and the gellation time as a function of the water content for PZT solutions, in which pH changes, influence the conversion of the gel to oxides. The solvent AcOH, or acetylacetone, significantly decreases the calcination temperature to 500 °C [10]. A perovskite phase is formed at a low temperature, 450–500 °C, along with a small amount of an intermediate pyrochlore phase [5]. To achieve PZT powders without the presence of a pyrochlore phase, a high calcination temperature is required (<600 °C).

Sol–gel processing is a method for the preparation of materials which offers the possibility of good compositional control in a multi-component system. In this work, a mixed lead titanyl zirconyl acetate precursor gel was prepared in an acidic solution by chelating a mixture of Pb, Zr and Ti alkoxides with acetic acid. The gel was after filtration dried and calcined to yield the [$Pb(Zr_{0.53}Ti_{0.47})O_3$, PZT] powder.

In this paper, the influence of the hydrolysis conditions, the AcOH concentration and the hydrolyzing factor on the polycondensation of acetate-alkoxide in the sol-gel process of PZT gels preparation and on the final stoichiometry of PZTphases obtained by calcination of almost pure PZT gels (unreacted organic precursors were removed by filtration of gels) have been studied.

2. Experimental

2.1. Preparation of PZT

PZT gels were prepared by sol-gel synthesis according to the scheme shown in Fig. 1. The basic precursors, lead acetate trihydrate $Pb(OAc)_2.3H_2O$ (analytical grade, Merck) and zirconium acetylacetonate $Zr(AcCHAc)_4$ ($Zr(OR)_4$, for synthesis, Merck), were dissolved separately at $T = 80$ °C in AcOH in two closed flasks. The solutions were dehydrated at 105 °C/2 h and after cooling to 80 °C they were mixed with the acetate solution of titanium orthotetrabuthylate $Ti(OC_4H_9)_4$ ($Ti(OR)_4$, for synthesis, Merck) in the required ratio of Pb:Zr:Ti = 1:0.53:0.47. By polycondensation of the formed orange lead zirconyl titanyl acetate precursor [$Pb(Zr)(Ti)(OAc)_x(OR)_y$], after adding a hydrolyzing agent [ethylene glycol, H_2O and NH_3(aq)] with the hydrolyzation ratio of 0.68–2.26 and the temperature of 80 °C, an yellow sol was formed, which was converted to a gel at the given temperature. Polycondensation took place in closed flasks. After polycondensation (12 h), the gels were filtered using a membrane filter (PVDF, Millipore, pore size <0.25 μm) to eliminate any non-condensed sol or unreacted organic precursor residuals. After drying at 100 °C/8 h, they were calcined at 500 °C/2 h in the air.

2.2. Testing methods

The stoichiometry of PZT phases was determined chemical analysis after dissolving calcinates in HCl (1:1) by complexometry (Pb, Zr) and colorimetry (Ti). The phase purity of the prepared PZT materials was determined by X-ray diffraction analysis (XRD) with an diffractometer Philips and infrared spectroscopy (IR) (Specord 80 M, CarlZeiss Jena). The decomposition kinetics of the dried gels during annealing was observed by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (derivatograph MOM 1500 Q, Budapest). The size and shape of particles of PZT phases were observed by transmission electron microscopy (TEM) (TESLA BS500). The specific surface of PZT calcinates was determined by N_2 adsorption at −196 °C (Gemini 2360).

3. Results and discussion

3.1. Studies of precursor

3.1.1. Chemical analysis

Gels (1,2,3 and 4) with various AcOH to (Pb + Zr + Ti) mole ratios (5.5, 7, 8 and 10) were pre-

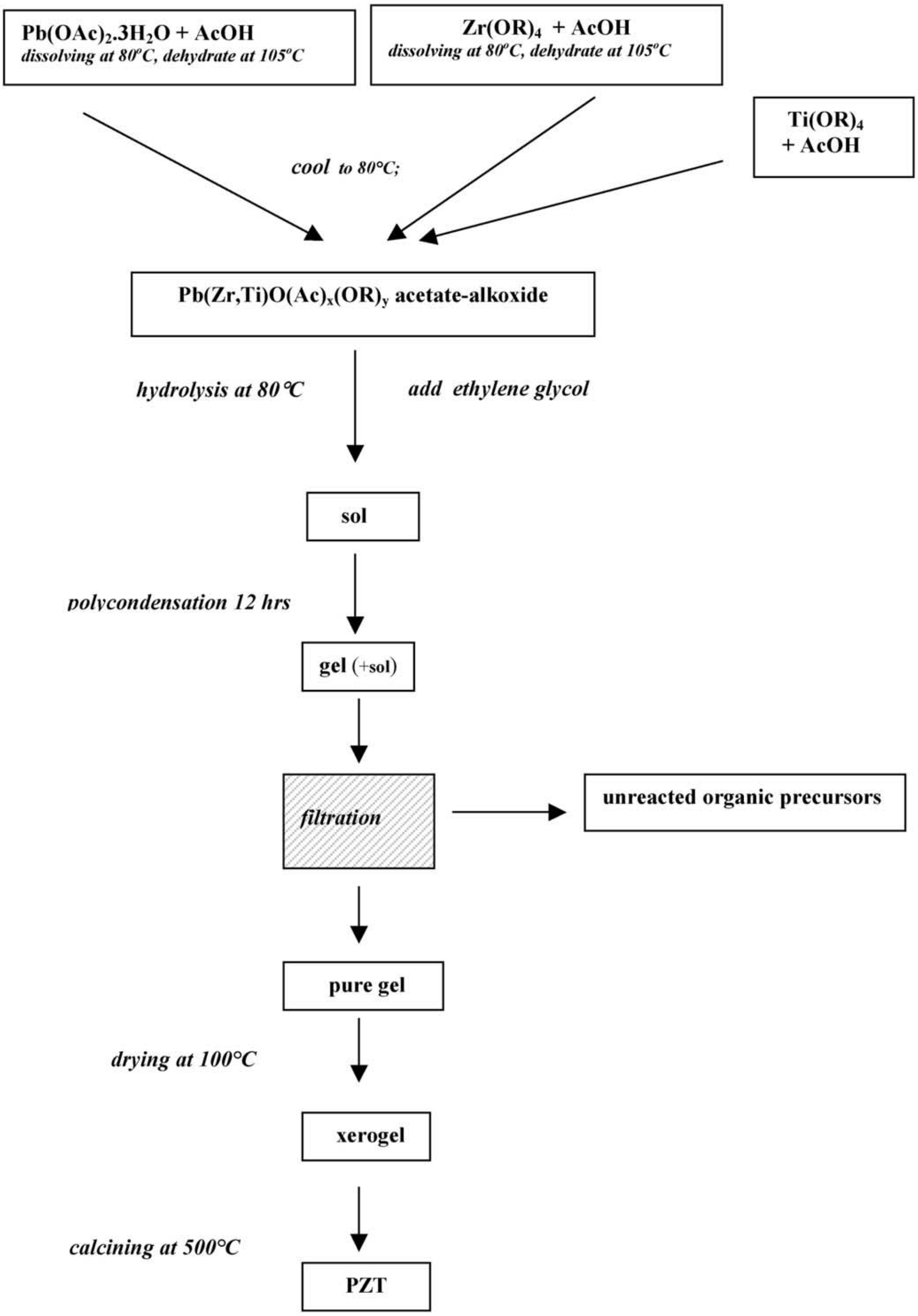


Fig. 1. Preparation route for the PZT powders sol-gel process.

pared by a sol–gel method and ethylene glycol was used as a hydrolyzing agent with the hydrolyzing factor $h = 0.68$. Gels (4,5,6,7,8 and 9) were prepared with a constant AcOH to (Pb + Zr + Ti) ratio and with various hydrolyzing agents; the gels (4, 5 and 6) with ethylene glycol ($h = 0.68$,1.36 and 2.26), the gels (7 and 8) with ethylene glycol + H_2O ($h = 1.56$ and 2.44) and the gel (9) with ethylene glycol + NH_3(aq) ($h = 1.58$).

Table 1 presents the results of chemical analysis of the prepared PZT calcinates and the yield values in wt.%. Calcinates prepared from gels 1 and 2 with a lower AcOH concentration had the average stoichiometry corresponding to the initial one, i.e. Pb:Zr:Ti = 1.0:0.53:0.47. The density and viscosity of these gels was high, which demonstrates a high polycondensation and crosslinking degree of individual gel

Table 1
Preparation conditions and stoichiometry of PZT calcinates obtained at 500 °C

Calcinate	Mole ratio (Pb + Zr + Ti): AcOH	Mole ratio ($C_2H_6O_2 + H_2O$ + NH_3(aq)) : PZT	Hydrol. factor (*h*)	Specific surface (m^2/g)	Colour	Yield *x* (wt.%)	$Pb(Zr,Ti)O_3$ stoichiom. ratio Pb : Zr : Ti
1	1 : 5.5	(0.68 + 0 + 0) : 1	0.68	2.63	Orange	86.25	1.01 : 0.54 : 0.46
2	1 : 7	(0.68 + 0 + 0) : 1	0.68	4.86	Orange	82.99	1.00 : 0.53 : 0.47
3	1 : 8	(0.68 + 0 + 0) : 1	0.68	9.19	Yellow	41.34	0.69 : 0.78 : 0.37
4	1 : 10	(0.68 + 0 + 0) : 1	0.68	15.26	Yellow	20.42	0.65 : 0.89 : 0.29
5	1 : 10	(1.36 + 0 + 0) : 1	1.36	19.15	Yellow	39.88	0.52 : 0.79 : 0.25
6	1 : 10	(2.26 + 0 + 0) : 1	2.26	11.16	Yellow	32.86	0.52 : 0.88 : 0.36
7	1 : 10	(0.68 + 0.88 + 0) : 1	1.56	6.03	Yellow	30.41	0.70 : 0.89 : 0.27
8	1 : 10	(0.68 + 1.76 + 0) : 1	2.44	6.52	Yellow	22.92	0.64 : 0.90 : 0.27
9	1 : 10	(0.68 + 0 + 0.90) : 1	1.58	8.39	Yellow	29.90	0.74 : 0.80 : 0.33

components. These gels were almost non-filterable, i.e. no filtrate was obtained by filtration. With an increasing acid concentration at a constant ethylene glycol concentration, the degradation of the starting stoichiometric ratio of cations in $Pb(Zr_{0.53}Ti_{0.47})O_3$ calcinate takes place, where in comparison with the initial stoichiometry the Pb and Ti contents decrease and the Zr content increases (gels 3 and 4). Thus, Pb and Ti are not completely bound in gel and they passes into filtrate.

The reactions describing the preparation process of PZT phases in the AcOH medium are summarized below:

$$\begin{aligned}&x\mathrm{AcOH} + \mathrm{Pb(OAc)_2.3H_2O} \\ &\quad + 0.53\mathrm{Zr(OR)_4} + 0.47\mathrm{Ti(OR)_4} \\ &\quad \rightarrow \left[\mathrm{Pb(Zr_{0.53})(Ti_{0.47})(OAc)_x(OR)_y}\right] \\ &\quad \text{stabilisation}\end{aligned} \tag{4}$$

$$\begin{aligned}&\left[\mathrm{Pb(Zr_{0.53})(Ti_{0.47})(OAc)_x(OR)_y}\right] + \mathrm{HOCH_2CH_2OH} \\ &\rightarrow \text{sol}\left[\mathrm{Pb(Zr_{0.53})(Ti_{0.47})(OAc)_x(OH)_y}\right] \\ &\quad \text{hydrolysis}\end{aligned} \tag{5}$$

$$\begin{aligned}&\text{sol}\left[\mathrm{Pb(Zr_{0.53})(Ti_{0.47})(OAc)_x(OH)_y}\right] \\ &\rightarrow \textit{gel}\ [\ldots \equiv \textit{T}\text{i-O-Pb-O-Zr} \equiv \ldots] \\ &\quad + \text{byproduct} \\ &\quad \text{polycondensation}\end{aligned} \tag{6}$$

$$\begin{aligned}&\text{xerogel}[\ldots \equiv \text{Ti-O-Pb-O-Zr} \equiv \ldots] \\ &\rightarrow \text{calcinate } \mathrm{Pb(Zr_{0.53}Ti_{0.47})O_3} \\ &\quad \text{pyrolysis}\end{aligned} \tag{7}$$

By a sol–gel process, hydrolysis and condensation polymerization reactions, a viscous gel is formed. AcOH was used for stabilization of alkoxides according to (4). After hydrolysis of heteroacetatealkoxides by ethylene glycol and polycondensation esterification (reactions 5, 6), esters form into chelate complexes. By pyrolysis reaction (7), decomposition of organic ligands takes place [11,12].

During dissolution of the organic precursors in AcOH, exchange of OR ligands in metallic alkoxides for acetate groups takes place, and the acetate groups enter the reactions (4,5,8,9) in the partially or fully acetized form [3,8,13].

$$\begin{aligned}&\mathrm{CH_3COOH + Ti(OC_4H_9)} \\ &\quad \rightarrow \mathrm{(CH_3COO)Ti(OC_4H_9)_3 + C_4H_9OH}\end{aligned} \tag{8}$$

$$\begin{aligned}&\mathrm{CH_3COOH + Zr(CH_3COCHCOCH_3)_4} \\ &\quad \rightarrow \mathrm{(CH_3COO)Zr(CH_3COCHCOCH_3)_3 + C_5H_8O_2}\end{aligned} \tag{9}$$

In the case of $Pb(OAc)_2$, which is only slightly ionized in solutions, further suppression of its ionization and hence reduction of its reactivity during polycondensation takes place, probably due to an increase of the AcOH concentration. It can be considered that the dissolubility of the prepared gels increases with an increase of the AcOH content (see the yields in Table 1). Acidic conditions tend to produce partially hydrolyzed monomers which condense into a more linear, lightly cross-linked network [7]. This fact is confirmed by the measured values of specific surfaces of PZT calcinate particles (Table 1). With the increase of the initial AcOH concentration (calcinates 1–4 in Table 1), the specific surface of PZT calcinate particles grows due to a decrease gel networking degree and hence the reduction of the distance between individual cations, which is crucial during calcination from the viewpoint of their reactivity and the sintering rate of the formed powder particles.

By adding H_2O or NH_3(aq) to ethylene glycol, the slowing-down of hydrolysis (gels 7, 8 and 9) and the degradation of the stoichiometry of PZT calcinates take place [4,7]. Water may be added along with an acid to further tailor these pore controlling reactions. Because water is usually a byproduct of a condensation, an addition of excess water can inhibit condensation and therefore shift the reaction toward further hydrolysis [8,13,14].

Similary by increasing the ethylene glycol concentration (increasing h from 0.68 to 2.26), causes the formation of nonstoichiometric PZT gels (see stoichiometry of calcinates 5 and 6 in Table 1) with a low Pb content. Increasing the hydrolysis temperature to 90 and 95 °C did not have a significant effect on the final stoichiometry of PZT calcinates. (Tartaj et al. recommend a longer polycondensation and gelling time at $T > 40$ °C [8,13].

3.1.2. DTA, TGA analyses

The results of DTA and TGA of the dried gels 2, 3 and 1 are shown in Fig. 2a–c. Two exothermic peaks at 250 and 440 °C can be seen in the DTA curve of the gel 2 (Fig. 2a), which correspond with the total weight loss of 44.3 wt.% in the TG curve, and a small endothermic peak (100 °C). A small decrease (~3 wt.%) is visible in the TG curve at 100 °C, which is due to elimination at residual water or volatile esters. The peak at 250 °C is characteristic at a decomposing oxyacetacylates group in the gel (weight loss of 31.8 wt.%), and at 440 °C the decomposition of the other organic ligands takes place (e.g. acetylacetonate group, weight loss of 8.7 wt.%). The exo-effect at 440 °C disappears at about 500 °C, and since no further heat effects or weight changes were observed in the DTA/TG curve up to 700 °C, the temperature of 500 °C represents a sufficient temperature for the formation of a perovskite phase from the respective gel.

Under similar preparation conditions to that used in this work (AcOH and ethylene glycol concentrations), 2 exothermic peaks at 350 and 430 °C were recorded in [9]—crystallization of PZT, and one exo-peak at ⩽500 °C was recorded in [14–16]. In [10,17,18], 3 exothermic peaks were observed in the DTA curves at 220–280, 350 and 435–490 °C. In the TG curve of gels, weight losses were observed at 140 °C—H_2O, 250 °C—elimination of the organics, 332 °C - decomposition of organic ligands [15] and 500 °C—formation of a crystalline phase [10].

The decomposition of the dried gel 3 (Fig. 2b) is characterized by three exo-effects in the DTA record at 260, 310 and 385 °C and by one endo-effect with the maximum at 90 °C, which correspond to the weight losses observed in the TG curve (4.1, 19 and 20.3 wt.%, and at the endothermic peak 6.4 wt.%, with the total weight loss of 49.4 wt.%). Organic ligands are practically eliminated at 400 °C, which is evidence of weak binding between organic ligands and metallic cations and is in accordance with the knowledge of a its lower crosslinking in gel. The presence of an endothermic peak at ~100 °C, which can be observed in the decomposition curve of $Pb(OAc)_2.3H_2O$, supports the possibility at occurrence in the non-reacted form in the gel.

Fig. 2c (gel 1) represents a mixed DTA and TG record from Fig. 5a and b, i.e. the formation of pyrochlore and perovskite phases, which is in accordance with the XRD diffraction analysis results. In the DTA curve, four exo-effects are recorded at 250, 280, 365 and 430 °C and one slight endoeffect at 90° with the respective weight losses in the TG curve. DTA analysis confirms the existence of two-phase regions in the gel. In the gel with a H_2O addition ($h = 0.68$), the TG curve shows a weight loss of 59.2 wt.% and the DTA curve shows 3 exothermic peaks at 100, 310 and 360 °C. No perovskite PZT phase was formed.

3.1.3. Infrared spectrum analysis

The gradual thermal decomposition of individual organic components of the gel 2 was observed by IR spectroscopy (Fig. 3Fig. 3A and B). The IR spectrum of

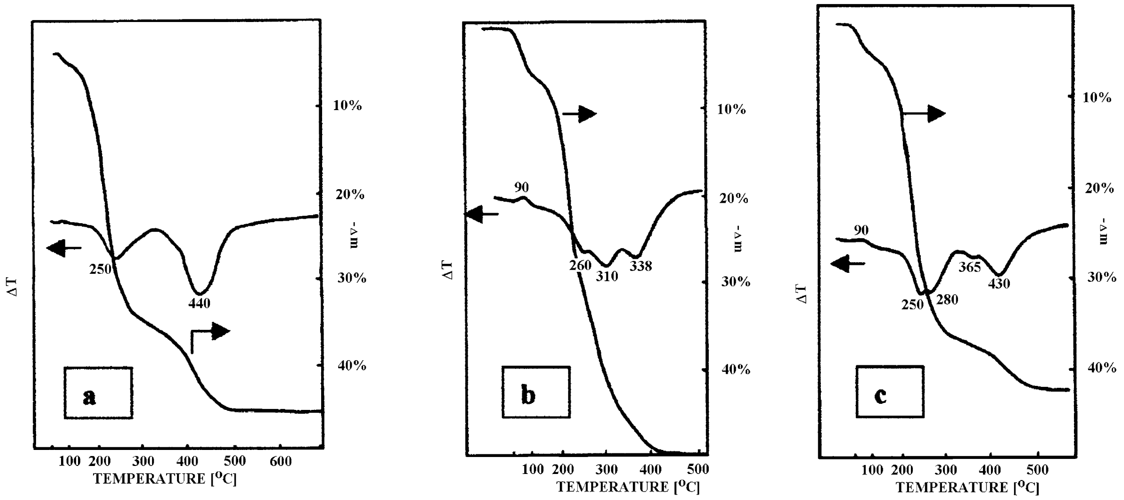
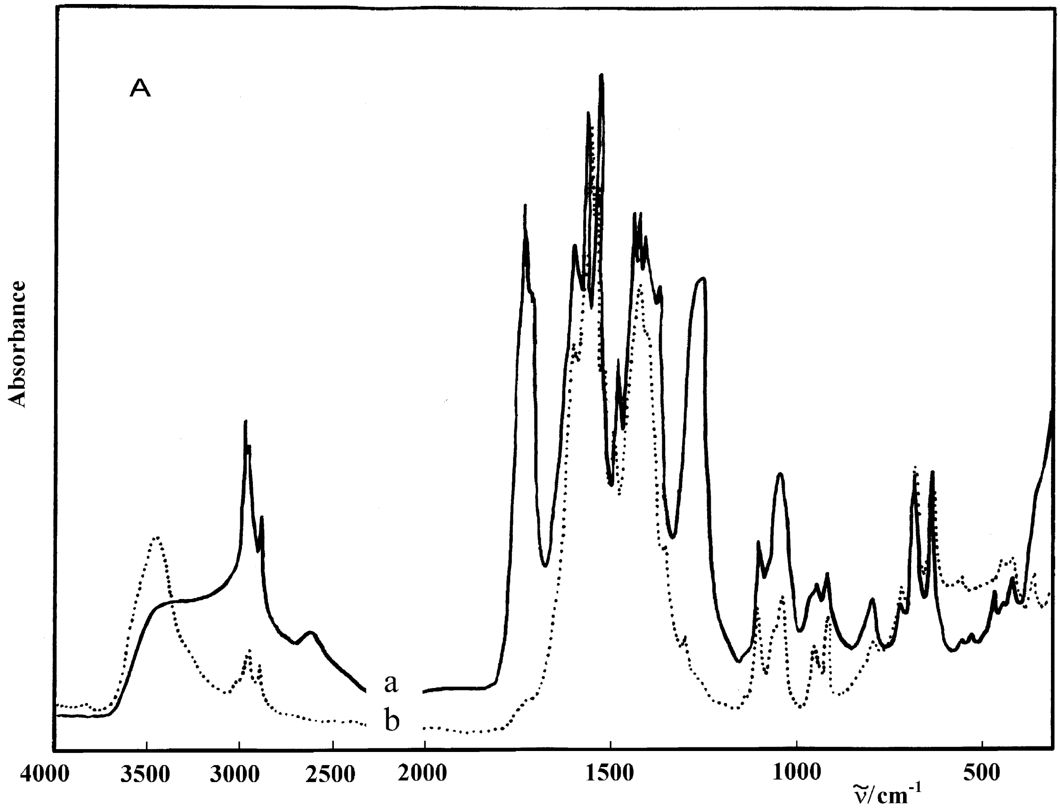


Fig. 2. DTA and TGA of dried gels: (a)-gel 2, (b)-gel 3 and (c)-gel 1.



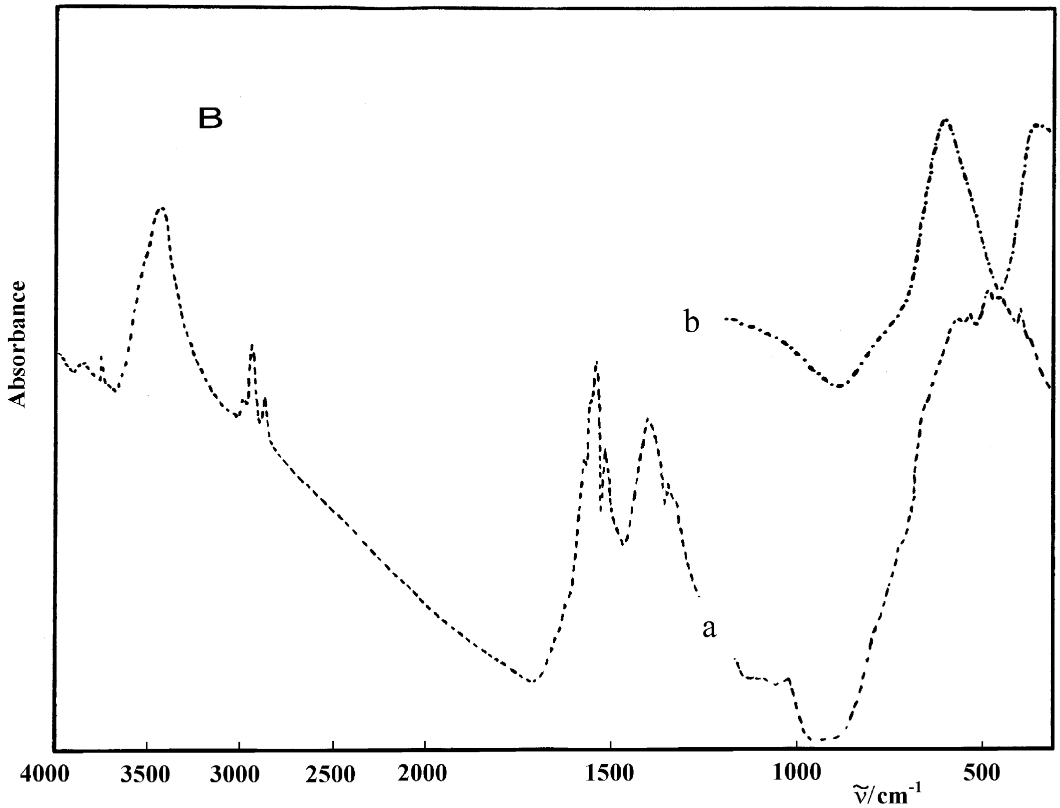


Fig. 3. IR analyses of prepared gels 2: A: (a) as-filtered, (b) as-dried at 100 °C; B: (a) as-annealed at 250 °C, (b) as-calcined at 500 °C.

the prepared gel (Fig. 3A a consists of bands corresponding to the presence of various organic ligands. The bands at 3100–3200 cm^{-1} characterize the valence vibrations of –OH groups; at 2900–3000 cm^{-1} the valence vibrations of –CH_2 and a –CH_3 groups; at 1700–1800 cm^{-1} valence vibrations of –C=O group in free acetic acid (similarly, the band at 1300 cm^{-1} characterizes the valence vibrations of –C–O, or deformation vibrations of –COO groups) and its esters; the bands at 1700–1300 cm^{-1} corresponding to the vibrations of the bound acetate CH_3CO-group to the metal cation mixed with the –C=O group spectrum in acetylacetonate. The band characterizing the valence vibrations of –C=O group of free acetic acid is significantly modified, which demonstrates that the acetyl group is actively involved in the gel formation, while CH_3COOR esters are formed. In [15,16], the authors recorded in the IR curves of PZT gels the presence of AcOR esters (1740 cm^{-1}), or chelate Zr and Ti complexes and their elimination, the formation of H_2O and free AcOH. It is evident from Fig. 3Ab that after drying at 100 °C two bands corresponding to the vibrations of –CO groups of free AcOH and its esters in the IR spectrum disappear. At the same time, the band characterizing the valence vibrations of –CH_2 and –CH_3 groups (about 3000 cm^{-1}), which are very intense in Ti butylate, also decreases, i.e. it can be concluded that volatile butylate AcOH ester is formed in polycondenzation. In the spectrum, peaks can be distinguished that can clearly be assigned to vibrations coming from acetylacetonate group vibrations (1592, 1528, 1480 cm^{-1}) and to valence vibrations of –C=O group (coming from the bound-Ac groups) laying at 1544 cm^{-1}. The band around at 1400 cm^{-1} corresponds to the mixed vibrations of acetylacetonate–AcCHAc and acetyl (–AcOH) groups. At the annealing temperature of 250 °C, a decrease of bands characteristic for the vibrations of acetylacetonate and bound acetylate groups takes place, while the vibrations of –OH groups and –CH_3 or –CH_2 groups are enhanced in the spectrum, which may correspond to stronger bonds with ethyleneglycol and to bound –OH groups. In the spectrum, a new, broad band can be observed at 800–300 cm^{-1} (Fig. 3Ba), which represents the formation of new M–O–M bonds, (M = Ti, Zr and Pb). The IR spectrum of a perovskite phase after calcination of the stoichiometric gel at 500 °C is shown in Fig. 3Bb.

3.1.4. XRD and TEM analyses

The average particle size of a perovskite phase of PZT calcinates determined by XRD diffractometry was 25 nm, which is in accordance with the particle size observed by TEM (Fig. 4). It is known from literature that in PZT calcinates, besides the prepared perovskite (pv) phase, an undesirable pyrochlore (py) phase is formed, which is mainly due to nonstoichiometry in the precursors [8–10]. Fig. 5 shows XRD diffraction patterns of the calcinates 1 and 2. It can be seen that in the calcinate 1 (the lowest AcOH concentration), with the retained initial stoichiometry of cations, a pyrochlore phase is present besides a perovskite phase, and hence a pure perovskite phase is not formed at a high molar ratio of (Pb + Zr + Ti) to AcOH at 500 °C. The formation of a pyrochlore phase takes place at an excess of ZrO_2 (or TiO_2) in relation to the PbO amount [15]. A low acid concentration causes an increase of pH of the solution, which consequently speeds up polycondensation of Zr and Ti, which have a greater tendency to hydrolyze in solutions under less acid conditions. As a result, two-phase regions are formed: one phase with high ZrO_2 and TiO_2 contents, which is formed during initial gellation stages, and the other phase with a high content of PbO, or its non-reacted residue occurring in the gel pores, which joins into the gel more slowly and at lower Zr and Ti concentrations in the sol (as a result of a lower polycondensation rate). The calcinate 2 with

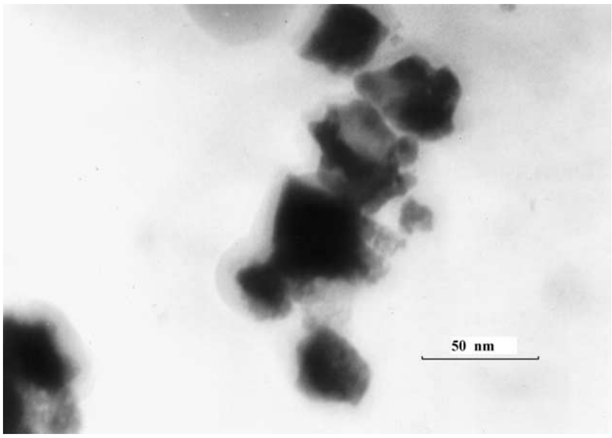


Fig. 4. TEM micrograph of PZT calcinate 1 from Table 1.

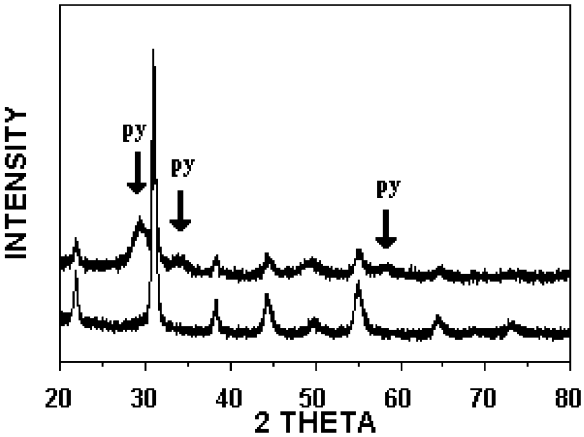


Fig. 5. XRD analysis of PZT calcinates with stoichiometric cation molar ratio prepared from gels at different AcOH concentrations: calcinate 1 (upper curve, lower AcOH concentration); calcinate 2 (lower curve, higher AcOH concentration). Arrows - pyrochlore phase.

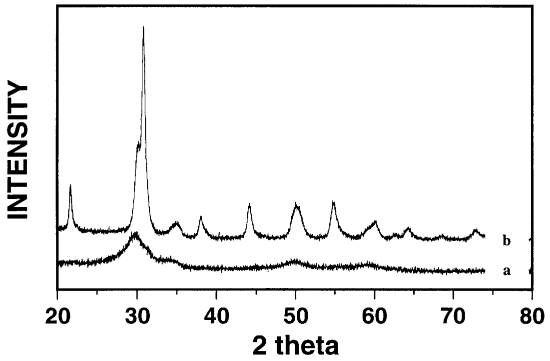


Fig. 6. XRD analysis of PZT calcinate 3 obtained at (a) 500 °C (upper curve) (b) as (a) and additionally annealed at 700 °C (lower curve).

a higher molar ratio of the cation sum to AcOH in comparison with calcinate 1 is composed of a pure perovskite phase.

The calcinates 3 and 4 with a nonstoichiometric cation ratio contained only a pyrochlore metastable phase (Fig. 6a). Due to an excess of H_2O as an esterification product, a secondary pyrochlore phase (Pb-deficient) with the composition $Pb(Zr,Ti)_3O_7$ is formed according to [15], which degrades the stoichiometry of the PZT calcinate. In references [15,19] it has been found out that the py phase content increases with H_2O content.

The XRD diffraction pattern of the calcinate 3 (Fig. 6b) after additional annealing at 700 °C/2 h in the air confirms the transformation of the original pure pyrochlore phase into the mixture of pyrochlore and perovskite phases. This verifies a lower stability of a pyrochlore phase, despite significant cation non-stoichiometry of the gel, which is in accordance with the knowledge of the py → pv phase transformation [12,15,19–21].

4. Conclusions

The results of experimental work can be summarized in the following points:

1. To prepare a viscous, polycondensed, stoichiometric PZT gel, the optimum molar ratio of $(Pb+Zr+Ti)$ to the solvent, acetic acid AcOH, is 1:7, with the hydrolysing factor of 0.68 and ethylene glycol as a hydrolysing agent. A pure perovskite phase $Pb(Zr_{0.53}Ti_{0.47})O_3$ is formed by calcination at 500 °C.
2. At a low AcOH concentration, two-phase regions are formed in the gel, which are demonstrated by the simultaneous formation of a perovskite phase and a metastable pyrochlore phase at the calcination temperature up to 500 °C.
3. A high AcOH concentration causes the decrease of the Pb and Ti contents in the gel and the formation of a pyrochlore phase up to 500 °C. The rise of the hydrolysing factor by adding H_2O or NH_3 (aq) to ethylene glycol results in the formation of a less viscous PZT gel with a degraded starting stoichiometry of Pb:Zr:Ti. At 700 °C, the partial decomposition of a pyrochlore phase and the formation of a perovskite phase takes place, despite significant cation non-stoichiometry in the gel, or in the annealed calcinate.

Acknowledgements

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