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Production of piezoceramic powders by the thermal two-stage process

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The present paper describes the production of lead zirconate titanate (PZT) with different additives and of lead metaniobate (PN) by means of the Thermal Two-Stage Process. This process, especially developed for the synthesis of multicomponent ceramic powders is characterized by the following: the starting constituents are liquid metalorganic precursors, such as alcoholates or acetates, which are converted to a homogeneous, multicomponent ceramic powder by spray drying the liquid precursors, resulting in an organic granulate, which is then followed by the thermal conversion of this organic powder into the final ceramic material. The resulting ceramic powder shows favourable properties with respect to homogeneity and further processing, e.g. pressing and sintering of compacts. The efficiency of the process will be demonstrated by the characterization of the piezoelectric properties of the sintered compacts.

1. Introduction

The Thermal Two-Stage Process represents a novel method for the production of homogeneous and very pure mixed-oxide ceramics [1, 2]. It supplements the variety of processes established for the production of piezoceramic powders, such as mixing and milling, the sol-gel process or the co-precipitation method [3–5]. Piezoceramic powders produced by this novel method are especially suited for new fields of application, where special requirements are to be met. In microsystems engineering, for example, where the increasing future application of piezoceramic microcomponents is expected, microscopic homogeneity and the chemical purity of the initial powders are the basic prerequisite for a reliably high production yield. First prototypes of lead zirconate titanate (PZT)/polymer ultrasonic transducers have been developed on the basis of a PZT powder produced by the Thermal Two-Stage Process [6].

The Thermal Two-Stage Process starts with a solution of the respective metal-organic compounds. It is converted into an easily handleble precursor powder by spray drying in the first process stage. In the second stage, this powder is converted into the oxide-ceramic powder desired by treatment in a high-temperature fluidized bed. The calcined powder can then be applied to produce the components desired by means of tape casting and stamping [7] or cold compaction with subsequent sintering.

Compared to conventional processes, this method has a number of advantages. On the one hand, the process allows the production of a high-quality powder and is rather simple. On the other hand, there are no limitations as far as the selection of possible products is concerned.

To illustrate the variety of ceramics that may be produced by the method described, production of PZT-based ceramics and lead metaniobates (PN) shall be presented. Special emphasis shall be given to the system lanthanum-doped PZT (PLaZT).

2. Experimental

The piezoceramics produced and the initial compounds selected are shown in Table I.

For the production of PZT ceramics, lead acetate is dissolved in methanol. Then, the other metal-organic compounds are added and the solution is heated under reflux for a period of 2 h. In the case of PN, the starting compounds are heated under reflux in acetic acid for a period of about 1 h. Subsequently, the respective solutions are converted into the precursor powder by spray drying at about 150 °C. For conversion into the ceramic powder, the precursor powder is then subjected to a multi-stage thermal heating program in a high-temperature fluidized bed under constant air flow. Maximum temperature is about 800 °C.

The powder produced is subjected to a short milling process. Then, 2 wt % organic additives are added as compaction and bonding agents (polyvinyl alcohol and polyethylene glycol). After this, spray granulation takes place. The granules obtained are compressed to the compacts desired. They are subjected to sintering in a powder bed of $PbZrO_3/PbTiO_3$ at 1150 °C for P(La, Nd)ZT or in a powder bed of PbO/Nb_2O_5 at 1250 °C for PN. As a result, compact ceramics are obtained.

In addition to chemical analysis by X-ray diffraction (Siemens D 500) and X-ray fluorescence analysis

TABLE I Produced ceramics and starting compounds

Designation	Composition	Starting compounds
PZT	$Pb(Zr_{0.54}Ti_{0.46})O_3$	Pb(IV)-acetate Zr-*n*-propoxide Ti-ethoxide
PLaZT[a]	$Pb_{1-3x/2}La_x(Zr_{0.54}Ti_{0.46})O_3$	Pb(IV)-acetate Zr-*n*-propoxide Ti-ethoxide La-*i*-propoxide
PNdZT	$Pb_{0.97}Nd_{0.02}(Zr_{0.54}Ti_{0.46})O_3$	Pb(IV)-acetate Zr-*n*-propoxide Ti-ethoxide Nd-acetate
PN	$PbNb_2O_6$	Pb(II)-acetate Nb-ethoxide

[a] PLaZT/1.5:$x = 0.015$; PLaZT/2: $x = 0.02$; PLaZT/2.5: $x = 0.025$; PLaZT/4:$x = 0.04$.

(Siemens SRS 303), the products are also characterized by a structural analysis using the scanning electron microscope (SEM, Jeol JSM 6400) as well as by a determination of the piezoelectric properties. To determine the physical properties, suitable compacts are produced first (pellets, diameter of 6–10 mm, height of 0.5–1.0 mm). They are contacted with gold or silver and polarized in silicone oil at a temperature of 80 °C (PZT) or 150 °C (PN). The electric fields applied varied between 2.5 kV/mm (PZT) and 3.0 kV/mm (PN). The polarization times are 15 min (PZT) and 30 min (PN), respectively.

The electrical properties (relative dielectric constant K_T, dielectric loss factor $\tan\delta$) are measured by means of an LCR measuring device of the type SR 720 (Stanford Research Systems Inc., USA) at a voltage of $U = 1$ V and a frequency of $f = 1$ kHz. The coupling factors k_t and k_p are determined dynamically in accordance with the IRE standard [8] using an impedance-phase analyzer of the type HP4194A (Hewlett Packard). For the determination of the piezoelectric modulus d_{33}, the direct piezoelectric effect under cyclic load (120 Hz) is measured using a Berlincourt Piezo-d_{33} measuring device of the type CADT3300 (Channel Products Inc., USA).

3. Results

3.1. P(La, Nd)ZT ceramics

During thermal treatment in the high-temperature fluidized bed under air, decomposition of the precursor powder obtained by spray drying takes place in several steps. The varying lanthanum or neodymium content has no influence on the decomposition behavior. The initial white powder starts to blacken at 300 °C. At this temperature, decomposition of the metalorganic compounds is followed by a reduction of Pb(IV) to Pb(II) and the formation of $Pb_2Ti_2O_6$. At a temperature of 550 °C, the color of the powder changes to yellow, which is due to the decomposition of the $Pb_2Ti_2O_6$ and the formation of the PZT crystallizing in the perovskite phase. At a temperature of 800 °C, the powder is yellowish and conversion of the precursor to PZT is completed. The diffractograms are shown in Fig. 1.

After sintering the respective ceramics, the compacts have densities exceeding 97% of the theoretical density (TD). Irrespective of the composition, all La- or Nd-doped ceramics exist in the tetragonal modification nearly exclusively. In undoped PZT, however, the rhombohedral phase predominates. The tetragonal phase can hardly be detected. Other phases besides the perovskite phase of the PZT could not be identified in any of the compacts. The X-ray diffraction analysis of undoped PZT in comparison with PLaZT and PNdZT with addition of 2 mol. %, respectively, is shown in Fig. 2. The results are in agreement with the phase diagram. For undoped PZT ($Pb(Zr_xTi_{1-x})O_3$) a phase boundary can be observed at a Zr fraction of $x = 0.52$ [9]. This phase boundary between the rhombohedral ($X_{Zr} > 0.52$) and the tetragonal phase ($X_{Zr} < 0.52$) is shifted towards a

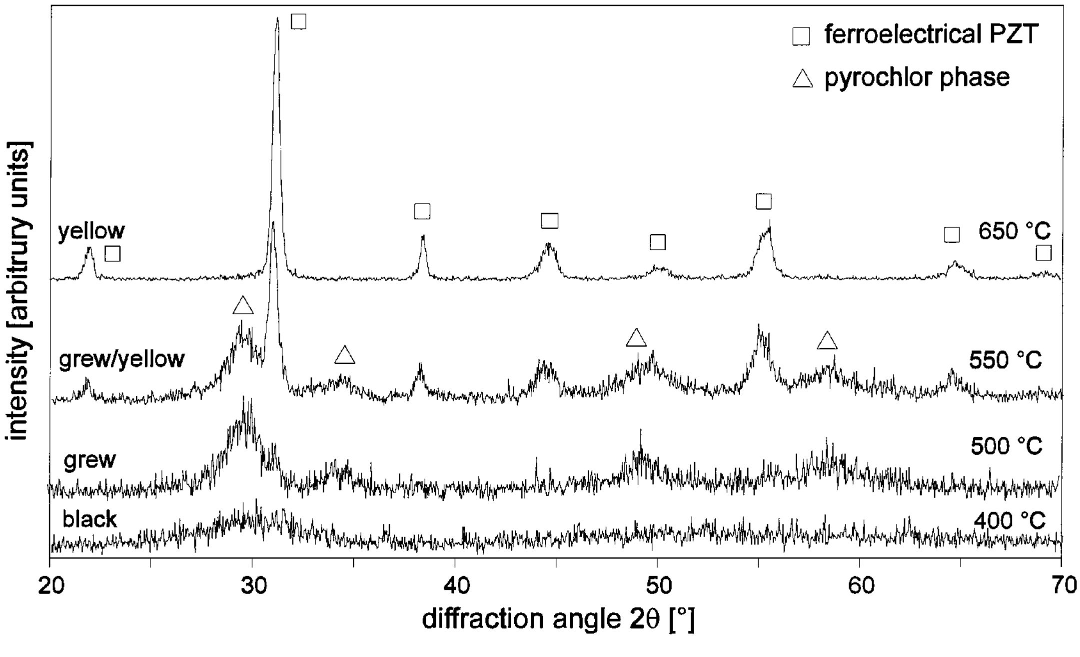

Figure 1 X-ray diffraction analysis of the decomposition products of PZT.

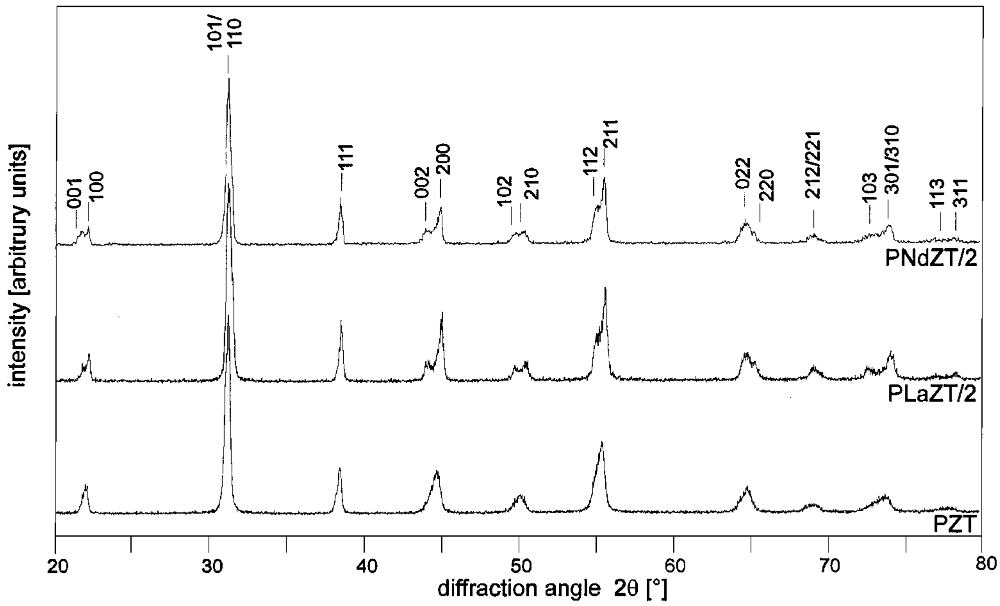

Figure 2 X-ray diffraction analysis of PZT, PLaZT/2 and PNdZT with *hkl* values; all specimens were subjected to sintering at 1150 °C for 1 h.

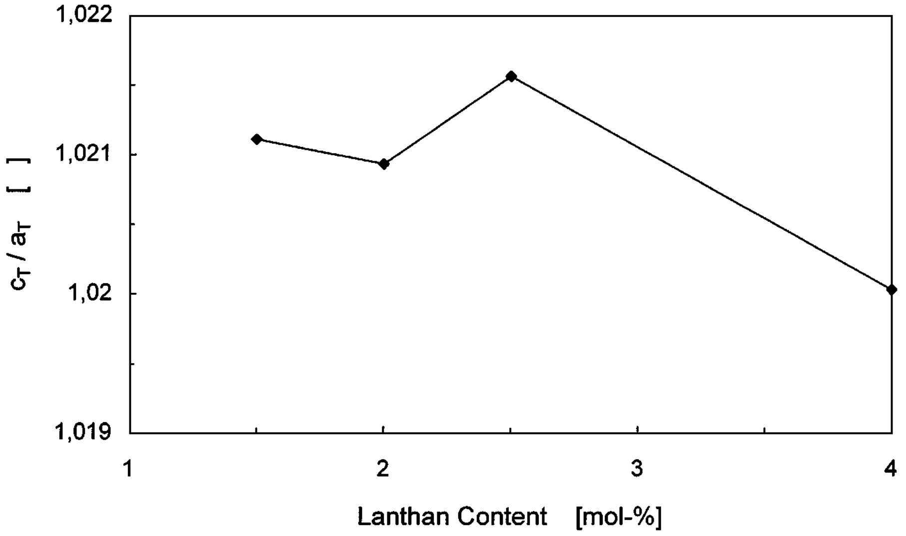

Figure 3 Distortion of the tetragonal phase of PZT and PLaZT as a function of the La doping content.

higher zirconium content with increasing doping of the perovskite structure with A-site donors, such as e.g. La^{3+} and Nd^{3+} [10]. By means of detailed X-ray structural analyses of the rhombohedral (200) and tetragonal (002) and (200) peaks in the 2θ angle range between 43 and 46.5°, the phase boundary of PLaZT was found to be exceeded already at less than 1.5% lanthanum. As expected, the ratio of the tetragonal lattice parameter c/a decreases with increasing lanthanum content, as shown in Fig. 3 [11].

The composition of the sintered ceramics, as determined by X-ray structural analysis, corresponds almost to the stoichiometry required in Table I. The mean grain size is approximately 1–2 μm for the undoped PZT and PLaZT/4 and varies between 2 and 5 μm for PZT with a lanthanum content of 1.5–2.5% (cf. Fig. 4).

The results of the physical characterization are presented in Table II. Maximum deviations of the individual specimens of a single charge were far below ±5% for the piezoelectric modulus and relative dielectricity, and less than ±10% for the other parameters.

TABLE II Piezoelectric properties of the ceramics

Material	Relative dielectricity constant	tan $\delta/10^{-3}$	k_p	k_t	d_{33} (pC/N)
PZT	550	8	0.45	0.47	195
PlaZT/1.5	1660	16	0.63	0.56	374
PlaZT/2	1600	18	0.72	0.51	447
PlaZT/2.5	1970	16	0.67	0.50	408
PlaZT/4	1420	12	0.48	0.45	256
PNdZT	1430	18	0.53	0.47	366

In Fig. 5, the coupling factor and the piezoelectric modulus are represented graphically for PZT with a lanthanum content of up to 4%. The strongest piezoelectric effect is observed at a lanthanum content of 1.5 to 2.5%, which is reflected by the height of the coupling factors and piezoelectric moduli. This is in agreement with the above X-ray structural analysis. While the undoped PZT with a zirconium content of $x = 0.54$ mainly exists in the rhombohedral modification, formation of the tetragonal phase is increased when the morphotropic

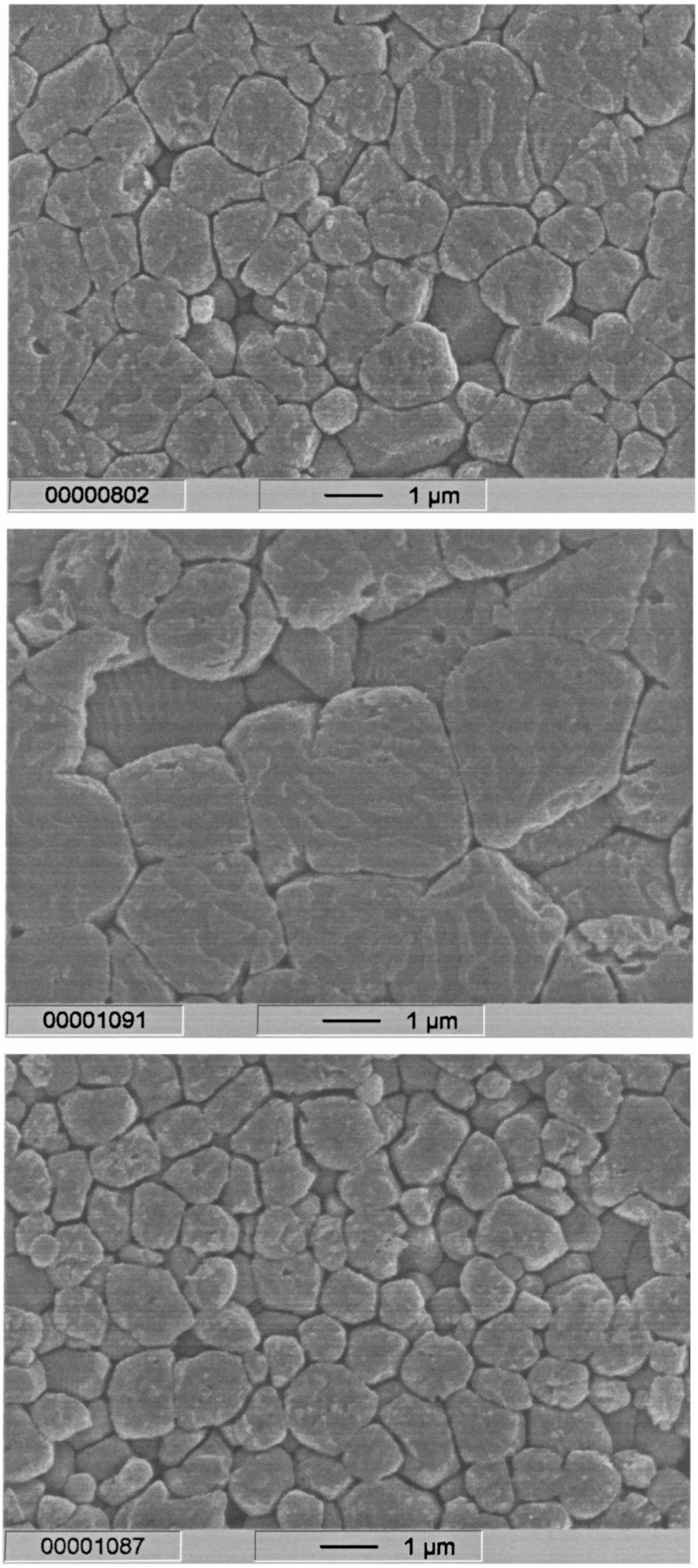

Figure 4 SEM micrographs (etched specimens) of PZT (above), PLaZT/2 (center) and PLaZT/4 (down).

phase range in A-site donor doping is exceeded. The distortion of the tetragonal phase (*c*/*a* ratio) and, hence, charge mobility in the perovskite lattice decreases with increasing doping. As demonstrated by X-ray structural analysis, the tetragonal phase fraction predominates in PLaZT with 1.5% lanthanum content already, i.e. the morphotropic phase boundary range has already been exceeded. Above a 2.5% La content, the piezoelectric effect decreases significantly, as expected.

3.2. PN ceramics

The sintering temperature of the lead metaniobate studied was set to 1250 °C. Hence, it is in the range of 1150 to 1250 °C, where the orthorhombically distorted, ferroelectric high-temperature modification of lead metaniobate is formed [12]. To achieve a metastable room temperature state without phase modification, the PN compact has to be quenched to below the Curie temperature of 570 °C after sintering. The existence of this

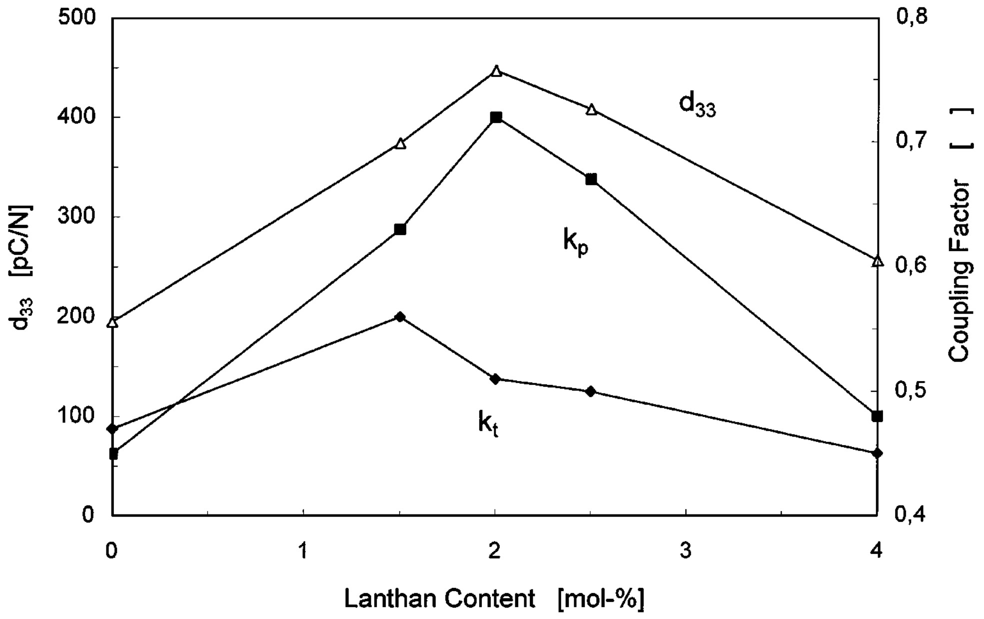

Figure 5 Piezoelectric modulus and coupling factors as a function of the La content, relative to the Pb sites in perovskite.

metastable ferroelectric phase can be demonstrated by subsequent X-ray structural analysis. Formation of the non-ferroelectric and at room temperature thermodynamically stable modification cannot be observed.

Densities of the sintered compacts were about 87–90% of the theoretical density. The piezoelectric properties (cf. Table II) of the ceramics are:

Piezoelectric modulus:	$d_{33} = 70$ pC/N
Transverse coupling factor:	$k_t = 0.34$
Relative dielectric constant:	$K^T = 245$
Mechanical quality:	$Q_M = 10$–20
Acoustic impedance:	$Z_A = 17.5\,10^6$ kg/m^{2}s

They are found to be nearly in agreement with the data given in the literature (e.g. [13]). As compared to the PZT materials studied, the scattering range of the piezoelectric modulus d_{33} of PN is much larger (deviations up to 30%). The planar coupling factor k_p of 0.25 is somewhat higher than in the literature, but comparable with the k_p values determined for several commercial lead metaniobate materials.

The stoichiometry determined by X-ray structural analysis is in agreement with the expectations. Mean crystallite size of the PN sintered compact is about 1–2 μm as for PZT.

4. Summary

The Thermal Two-Stage Process allows the simple production of a variety of piezoceramic powders with favorable physical properties. This could be demonstrated both for PZT-based and PN-based ceramics.

As far as the PZT ceramics are concerned, the PLaZT/2 material is characterized by a high planar coupling factor k_p and a high piezoelectric modulus d_{33} and relative dielectricity constant at a low loss angle tan.

The Thermal Two-Stage Process is especially suited to the synthesis of lead metaniobate of high purity and density with a defined stoichiometry. Even without a further material optimization, the physical material data are comparable with both literature data and the material data of commercial PN materials.

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