

Manufacturing and characterization of piezoceramic lead metaniobate PbNb_2O_6

S. RAY, E. GÜNTHER, H.-J. RITZHAUPT-KLEISSL
*Forschungszentrum Karlsruhe GmbH, Institut für Materialforschung III, Postfach 3640,
 D-76021 Karlsruhe, Germany*
E-mail: sikha.ray@imf.fzk.de

The synthesis of single-phase lead metaniobate powders by a novel Thermal Two-Stage Process is described. Ceramic parts are produced from these powders by dry pressing and sintering. Following polarization, the piezoelectric properties of the specimens are measured. The piezoelectric material data of the specimens from this novel processing route are comparable with the values known from literature.

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1. Introduction

In comparison with the far better known class of lead-zirconate-titanate ceramics (PZT), lead metaniobate shows a less distinct piezoelectric effect with respect to the piezoelectric charge constant (or piezomodulus) d_{33} . An advantage of lead metaniobate is the high bandwidth that is reflected by the extremely small value of the mechanical quality factor Q_m [1–3]. Furthermore, the strong directional anisotropy of the coupling coefficients k and piezomoduli d are important: In contrary to high values in the direction of the polar axis, the values perpendicular to it are negligibly small [1–3]. Another parameter of great interest is the high Curie temperature T_c of undoped, stoichiometric lead metaniobate of 570°C, which allows higher operating temperatures of the material than PZT – ceramics [1–3].

Lead metaniobate exists in a number of stable and metastable phases [2–4], but only the metastable phase derived from the tetragonal high-temperature phase by orthorhombic distortion exhibits piezoelectric properties [2, 3]. This is achieved by reheating the already calcined powder to a temperature above the formation temperature of the tetragonal phase of 1150–1175°C and subsequent quenching to below the Curie temperature $T_c = 570^\circ\text{C}$. Thus, formation of the stable, but not piezoelectric rhombohedral low-temperature phase is prevented. Instead, the crystal lattice turns into the orthorhombic phase when the Curie temperature T_c is reached [2, 3].

The piezoelectric properties of lead metaniobate are described in the literature [1–3]. There is a large scatter between the data, due to the fact that synthesis and especially ceramic processing of lead metaniobate still cause considerable problems [1]. In most cases, synthesis is performed by the mixed-oxide process (MO – process) taking the single oxides as raw materials, milling them together and reacting them in a high temperature solid state process [5–7]. In contrary to this classical MO – synthesis, the Thermal Two-Stage Process uses

liquid metal organic precursors, converting these chemically pure starting materials in two steps – spray drying and subsequent fluidized bed calcination – into the desired stoichiometric multinary oxides [8, 9]. In this respect, the Thermal Two-Stage Process represents an efficient method to produce material of the required purity and homogeneity. The powders obtained from this process can be easily handled, processed, formed by dry pressing and are suitable for sintering of ceramic parts. A ceramic and physical characterization of these parts will be presented below.

2. Experimental

2.1. Specimen fabrication

The ceramic lead metaniobate powder is synthesized by the Thermal Two-Stage Process [8, 9]. Niobium pentaethylate ($\text{Nb}(\text{OC}_2\text{H}_5)_5$) and lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$) are used as starting materials. A precursor solution is generated first by mixing and chemical conversion of these liquid precursors. Subsequently, the precursor powder is produced by spray drying of the precursor solution. This precursor powder is converted in a second step into the pure stoichiometric multinary oxide ceramic powder by calcination at 700°C for one hour in a fluidized bed furnace. A processing scheme is given in Fig. 1.

The produced powder is heated to 1250°C for 1 hour and quenched in ambient air in order to obtain the development of the piezoelectric phase. Then it is ceramically processed and characterized with respect to phase content, particle size distribution and specific surface according to BET. Subsequently, cylindrical pellets are prepared by dry pressing. These are sintered in ambient air at 1280°C for 2 hours. The sintered specimens are then characterized with regard to their phase content using X-ray diffraction (XRD). Their chemical composition is examined by X-ray fluorescence analysis. The bulk density of the samples was measured

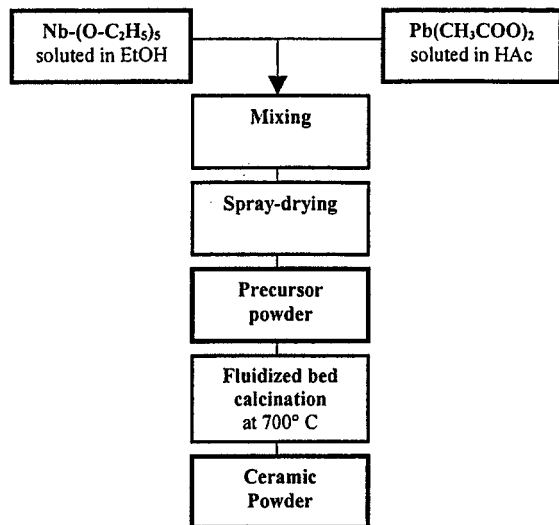


Figure 1 Processing scheme of the Thermal Two-Stage Process.

geometrically. The microstructure is analyzed by means of light microscopy and scanning electron microscopy of the polished and etched specimens.

2.2. Electrical characterization

To achieve the piezoeffect, the normally statistically distributed electric domains have to be oriented by a polarization process. For this purpose, the pellets are subjected to surface grinding and contacted with conductive silver varnish on the front surfaces, which is burned in for a period of 1 hour at 140°C. Polarization takes place in silicone oil at a temperature of 150°C by application of an electric field of 4 kV/mm for a duration of 90 minutes. After this, the piezomodulus, d_{33} , using a Berlincourt measuring device (CADT 3300, manufacturer: Channel Products Inc., USA) at a low cycling frequency of 120 Hz is measured.

Following final dimensioning (by cutting the pellets into thin slices, thickness around 280 μm), grinding and contacting of the specimens, further parameters can be determined for the characterization of the electric properties. These are: The resonance frequencies f_r and the antiresonance frequencies f_a which are determined by impedance spectroscopy. This is done dynamically using an impedance-phase analyzer of the type HP 4194A of Hewlett Packard, which measures the impedance and phase angle of the polarized specimen over a given frequency range. From the characteristic frequencies measured, the frequency constants N , the coupling coefficients k , the mechanical quality factor Q_m , the (resonant) piezoelectric charge constants d and the piezoelectric voltage constants g can be calculated. The capacity C , the dielectric loss $\tan \delta$ as well as the relative dielectricity constant ϵ_r are measured at an alternating voltage of 1 V and a frequency of 1 kHz using an LCR measuring device (SR 720, manufacturer: Stanford Research Systems Inc., USA). The (low-frequency) piezoelectric charge constant d_{33} and the piezoelectric voltage constant g_{33} are obtained by measuring the direct piezoelectric effect under cyclic loading at a low cycling frequency of 120 Hz using a

Berlincourt- d_{33} measuring device (CADT 3300, manufacturer: Channel Products Inc., USA).

3. Results

3.1. Ceramic characterization

Results of the ceramic characterization are given in Table I below:

According to chemical X-ray fluorescence analysis, the composition of the sintered specimens is 44.6 wt.% PbO and 54.9 wt.% Nb_2O_5 (totally 99.5 wt.%). This nearly corresponds to the theoretical composition of lead metaniobate of 45.64 wt.% PbO and 54.36 wt.% Nb_2O_5 . Consequently, evaporation of lead oxide during sintering is rather small as compared to PZT materials [2, 3].

X-ray diffraction of the powders and sintered parts reveals the purely rhombohedral phase for the powder calcined at 700°C. After phase transition annealing at 1250°C, pure-phase orthorhombic lead metaniobate is generated (ASTM 11-122). Following sintering, phase development becomes even more distinct (Fig. 2).

The sintering conditions selected (1280°C/2 hours) lead to geometrically determined sintered densities of 85–89% of the theoretical density. Light-microscopic investigations reveal a homogeneously distributed porosity. According to the investigations of the microstructure by means of scanning electron microscopy of the polished etched specimen, the pores are distributed homogeneously at the grain boundaries. The maximum grain size lies at about 10 μm (Fig. 3).

3.2. Electric characterization

The piezoelectric material data of lead metaniobate synthesized by the Thermal Two-Stage Process, as described above (PN 2/3) are given in Table II. The material data of two formerly commercially available lead metaniobates (Pz35, manufacturer: Ferroperm, Denmark and PN1, manufacturer: Morgan Matroc, UK) as well as several lead metaniobate data from literature are given for comparison and better evaluation:

TABLE I Ceramic material data of lead metaniobate

<i>Powder:</i>		
<i>Phase content</i>		
Before phase transformation heating		rhombohedral PbNb_2O_6
After phase transformation heating		orthorhombic PbNb_2O_6
<i>Particle size distribution</i>		
d_{50}	μm	13
d_{90}	μm	31
<i>Specific surface</i>	m^2/g	0.66
<i>Pellets:</i>		
<i>Green density</i> ρ_{green}	g/cm^3	4.94
<i>Bulk density</i> ρ_{bulk}	g/cm^3	5.77
	% th.D	87.2
<i>Linear shrinkage</i>	%	7.1
<i>Mass loss</i>	%	0.87
<i>stoichiometry</i>		44.6 wt.% PbO 54.9 wt.% Nb_2O_5
<i>Phase content</i>		orthorhombic PbNb_2O_6

TABLE II Piezoelectric material data of selected lead metaniobates

Properties	Symbol	Unit	PN-2/3	Pz35[10]	PN1[11]	PN[1]	PN[2]*
<i>Electric properties</i>							
Dielectricity constant	ϵ_r		287.9	220	275	285	195/225/280
Loss factor	$\tan \delta$	10^{-3}	10.25	6		10	
Curie temperature	T_c	$^{\circ}\text{C}$		500	495		
<i>Electromechanical properties</i>							
Coupling coefficients	k_p		0.196			0	/0.045/
	k_t		0.26	0.34		0.22	0.43/0.38/ 0.41(0.26)
Charge constant	d_{33}	pC/N	53.9	100	65	68	73/85/83
Voltage constant	g_{33}	MVm/N	19	43	27		42/42.5/
Frequency constants	N_t	MHzmm	1.757	1.550	1.525		
<i>Mechanical properties</i>							
Density	ρ	g/cm^3	5.66	5.60	6.000		/(6.33)
		% th.d.	84.9	84.6	90.6		/(95.6)
Quality factor	Q_m		22.5	15	15	10	Very small/11/

*Taken from Jaffe/General Electric/Goodman (in this order).

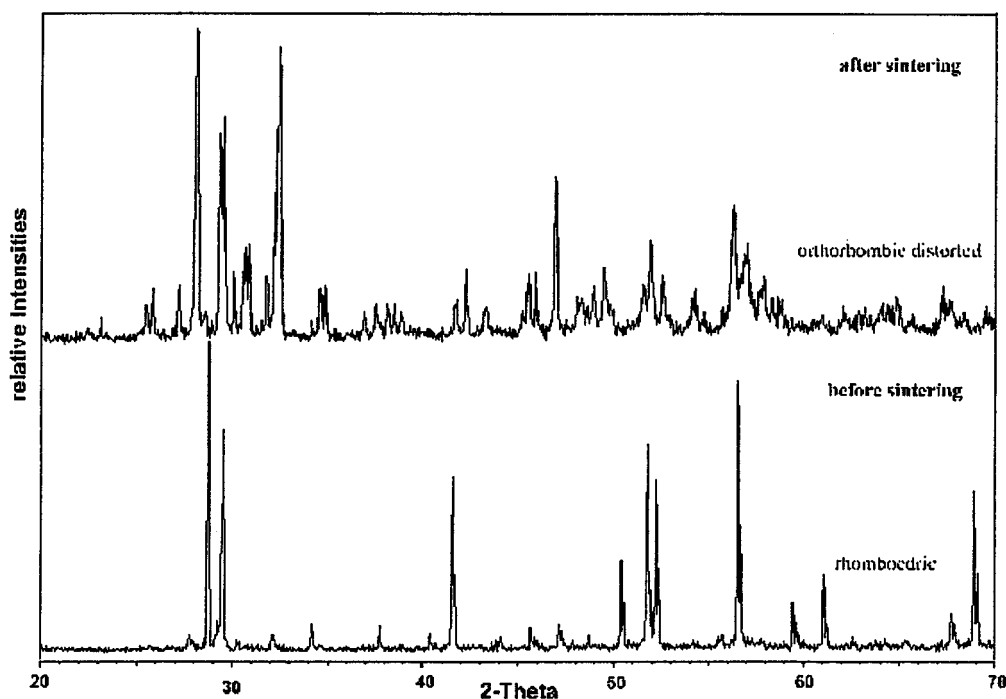


Figure 2 Phase content before and after sintering and quenching.

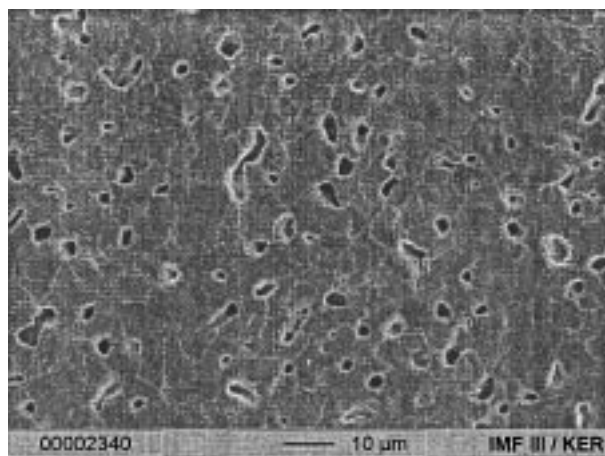


Figure 3 Scanning electron microscopy of the microstructure.

4. Discussion

When comparing the electrophysical measurements of our materials synthesized by the Thermal Two-Stage Process with the values known from literature [1, 2],

good agreement is observed with the values measured by Eyraud *et al.* [1] at least, who used materials produced by a coprecipitation process. This especially applies to the values of the dielectricity constant, the loss and the effective coupling coefficient, whereas the value of the charge constant still deviates considerably from the literature value. Harmonization may be achieved by an optimization of the polarization process towards a maximum piezomodulus. Compared to the material described in [1], the mechanical quality of our material also is remarkably high, which is attributed to the lacking bandwidth.

The values given in [2] originate from different sources. Their fluctuations are accordingly high, although pure lead metaniobates are used in all cases. The value of the dielectricity constant of the lead metaniobates produced by the Thermal Two-Stage Process is in good agreement with the dielectricity constant of the material described by Goodman, but differs considerably from that of the General Electric material and that of the material synthesized by Jaffe.

Compared to the literature values, the charge constant of the materials of our processing route seems to be rather low, which again may be attributed to the polarization process not optimized in this respect. The coupling coefficient in thickness direction of the sample, k_t , of our material therefore is also lower compared to the data taken from literature. It must be noted, however, that the value of 0.26 given by Goodman in his original work is in agreement with the coupling coefficient k_t of the material produced by the Thermal Two-Stage Process. As far as the planar coupling coefficient is concerned, a preliminary value only is obtained from the General Electric data sheet. But it is obvious that the value of the material produced by our processing route is rather high. Also for mechanical quality, only the value given by General Electric is available. It is far smaller than that of the materials produced by the Thermal Two-Stage Process.

When comparing the piezoelectric data of our samples with those of commercial suppliers, as taken from their data sheets, one has to bear in mind, that any comparison between these data is very difficult, as long as the experimental and measuring conditions are unknown. Furthermore, there is no information available of the composition of these materials. The Curie temperature for the Pz35 and for the PN1 are unusually low for pure lead metaniobate. This may be an indication that both materials are not pure lead metaniobate but are modified by some dopants. With respect to the Pz35 also the extremely high charge constant d_{33} of 100 pC/N may be a hint in this direction.

A complete set of piezoelectric data is not available for the commercial materials as can be seen from Table II. It was not possible to complete or verify these data, as due to experimental difficulties these materials are not produced and therefore not available any more. As far as these data are accessible, the measured values of our materials from the Thermal Two-Stage Process and those of the data sheet are of comparable level. The material of our own production by the Thermal Two-Stage Process differs from the commercial materials by a somewhat increased loss $\tan \delta$ of 10.25×10^{-3} as compared to 6×10^{-3} of the respective Ferroperm material. Furthermore the value of the charge constant d_{33} and, hence, of the effective coupling coefficient k_t of our material is somewhat below the values of the materials from commercial suppliers. The comparatively low charge coefficient d_{33} may be attributed to the polarization process which has not been optimized yet in terms of a maximum piezoelectric effect. The frequency constant N of 1757 Hzm of our material is higher than the values obtained for the reference materials of 1550 Hzm and 1525 Hzm, respectively. The frequency constant N is a measure of the acoustic density of a material and, consequently, determines the acoustic coupling behav-

ior. But it cannot be related directly to the mass density $\rho = m/V$. In comparison with the commercially available materials, the mechanical quality of our material is higher, e.g. resonance takes place at a more sharply defined excitation frequency than that of the reference materials. Hence, the material produced by the Thermal Two-Stage Process exhibits a smaller bandwidth.

5. Summary

The Thermal Two-Stage Process allows to perform the difficult synthesis of lead metaniobate with the stoichiometry being in good agreement with the theoretical composition. In this process by use of liquid initial substances, a mixture on an atomic level and, hence, very homogeneous precursor powders can be obtained. By the use of synthetic and chemically pure initial materials impurities that cannot be avoided in conventionally processed ceramics are excluded by this processing route and precursor powders of high purity are obtained. As compared to the synthesis methods described in literature (mixed-oxide process, coprecipitation process etc.), in this process not only impurities are avoided but also the process times are reduced considerably with the desired ferroelectric orthorhombic phase of sufficient purity being maintained. Although the polarization process has not yet been optimized in terms of maximum piezoelectric properties, the piezoceramic material data of the sintered specimens are comparable with the values known from literature.

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