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Powder process influence on the characteristics of Mn,W,Sb,Ni-doped PZT

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Abstract

The use of lead zirconate titanate ceramics for applications like actuators implies the development of materials with high mechanical quality factor Q_m and high electromechanical coupling coefficient k_p. The composition $Pb((Zr_{0.49}Ti_{0.51})_{0.94}Mn_{0.0252}Sb_{0.0192}W_{0.0156})O_3+0.2$ wt.% NiO has been studied with this aim in view. Homogeneous, fine and desagglomerated powders are required. A new doped PZT powder elaboration process by hydrothermal route has been developed. The same composition is also prepared by a conventional calcination route. The chemical and physical characteristics of these two kinds of powders are studied and the sintering behaviour has been investigated. Ceramics from the hydrothermal route densify at 850°C while the ceramics from the calcined powders require a sintering temperature of 1150°C. The microstructures were studied and the piezoelectric and ferroelectric properties were determined. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical properties; Microstructure-final; Piezoelectric properties; Powders-chemical preparation; PZT

1. Introduction

Generally, PZT powders are synthesised by a calcination route followed by a desagglomeration step.[1,2] Lowering of the PZT ceramic sintering temperature has been studied by many authors. Different methods are reported : the use of additives to form liquid phases,[3,4] the development of the chemical powder process[1] like sol–gel,[5] coprecipitation,[6] hydrothermal[7,8] route which lead to fine reactive and homogeneous powders.

The aim of this work is to determine the powder process influence on the ceramic properties for actuator applications. The composition $Pb((Zr_{0.49}Ti_{0.51})_{0.94}Mn_{0.0252}Sb_{0.0192}W_{0.0156})O_3+0.2$ wt.% NiO presents high mechanical quality factor (Q_m) and high piezoelectric constant (d_{33})[9] which are necessary for actuators. A new hydrothermal route for codoped PZT powders synthesis has been developed. The same composition has also been prepare by the calcinated conventional route. A short study of milling influence after powder calcination is presented. Resultant ceramic piezoelectric properties are compared.

2. Experimental procedure

2.1. Calcined powders

The commercial powders PbO, ZrO_2, TiO_2, $MnCO_3$, Sb_2O_3, WO_3 and NiO were used as raw materials. After weighing, the mixture is homogenised by ball milling in MEK-ethanol medium for 2 h, dried, sieved and calcined at 820°C for 5 h. The PZT powders are then milled in a two step milling process: 6 h dried ball milled and, thereafter, 6 h milled in MEK-ethanol media. In the aim to evaluate the importance of the secondary wet milling, powders are sintered after the first milling step (sintering A) and after the second milling step (sintering B).

Several calcined powders have been prepared with different compositions in the aim to determine the influence of Ni-adding and PbO excess influences. Calcined powder compositions are reported in Table 1.

2.2. Hydrothermal powders

A clear solution of mixed titanium isopropoxide, zirconium propoxide and antimony ethoxide is prepared in isopropanol. Once hydrolysed, the tungsten chloride solution is added and the suspension is mixed for 2 h. The precipitate is filtered to eliminate alcohol. The fresh

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Table 1
Powder theoretical composition

Name[a]	Powder composition
C1	$Pb((Zr_{0,49}\ Ti_{0,51})_{0,94}\ Mn_{0,.0252}\ Sb_{0,0192}\ W_{0,0156})O_3$
C1N	$Pb((Zr_{0,49}\ Ti_{0,51})_{0,.94}\ Mn_{0,0252}\ Sb_{0,0192}\ W_{0,0156})O_3 +$ 0.8758% mole Ni
C2	$Pb_{1,03}((Zr_{0,49}\ Ti_{0,51})_{0,94}\ Mn_{0,0252}\ Sb_{0,0192}\ W_{0,0156})O_3$
C2N	$Pb_{1,03}((Zr_{0,49}\ Ti_{0,51})_{0,94}\ Mn_{0,0252}\ Sb_{0,0192}\ W_{0,0156})O_3 +$ 0.8758% mole Ni
H1	$Pb((Zr_{0,49}\ Ti_{0,51})_{0,.94}\ Mn_{0,0252}\ Sb_{0,0192}\ W_{0,0156})O_3$
H2	$Pb((Zr_{0,49}\ Ti_{0,51})_{0,94}\ Mn_{0,0252}\ Sb_{0,0192}\ W_{0,0156})O_3 +$ 0.8758% mole Ni
H3	$Pb((Zr_{0,49}\ Ti_{0,51})_{0,94}\ Mn_{0,0252}\ Sb_{0,0192}\ W_{0,0156})O_3 +$ 0.8758% mole Ni

[a] C1, C1N, C2 and C2N are calcined powders; H1, H2 and H3 are hydrothermal powders.

precipitate is then redispersed in water. Aqueous solutions of lead nitrate, with an excess of 30%, and manganese nitrate are added. KOH pellets are then introduced, final KOH concentration is 1 mol·l^{-1}. Hydrothermal treatment is performed for 2 h at 265°C, under an autogenerated pressure of ≈45 bars. After the treatment, powder is filtered and washed. The aqueous solution of nickel nitrate is then added, the suspension is mixed for 10 min and oven dried.

Hydrothermal powder compositions are reported in Table 1.

2.3. Sample preparation

The powders were pressed isostatically at 300 MPa. Dilatometric characterisation was performed at 5°C min^{-1}, from 20 to 1300°C, under a protective atmosphere to prevent lead volatilisation. The ceramics were sintered at the temperature corresponding to the maximum of densification rate for 2 h. PZT powder was used as an atmosphere buffer. For electrical measurements, pellets were sampled at the ceramic heart, with thickness of 1 mm, polished and cleaned in acetone. Silver pastes were coated to form electrodes on both sides of the sample, and fired at 650°C for 30 min. The samples were polarised under 3.5 kV/mm^2 applied voltage at 80°C in an oil bath for 1 h.

2.4. Characterisations

The homogeneity of the PZT solid solution was determined for sintered samples by means of high temperature X-ray diffraction measurements (Siemens D5000 θ-θ) described in a previous work.[10]. The microstructures were analysed on chemically etched samples by SEM. The mean grain size was determined by the linear intercept method.[11]

2.5. Electric measurements

The dielectric measurements were performed using a 4192A Hewlett Packard impedance analyser at room temperature at 1 kHz, 0.2 V. The piezoelectric properties of samples were measured after being polarised and stabilised for 24 h, and electromechanical characteristics were calculated from the resonance measurements.

3. Results and discussion

3.1. Sintering behaviours

Sintering behaviours for calcined and hydrothermal powders are presented in Fig. 1.

Calcined powders densify over a broad temperature range. On the contrary, hydrothermal powders densify in a sharp temperature range which indicates a homogeneous reactivity.

The C1 and C1N samples are fully densified above 1050°C. The powders with lead excess C2 and C2N are

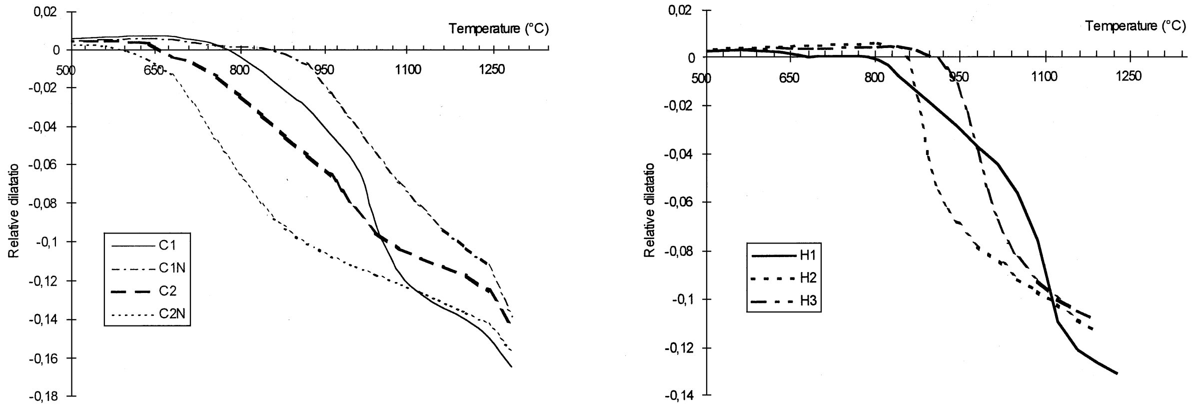

Fig. 1. Sintering behaviour; (a) calcined powders; (b) hydrothermal powders.

the most reactive. Sintering occurs at 1000°C for C2 and 850°C for C2N.

For the hydrothermal powder H1 sintering occurs at a high temperature (above 1100°C) but Ni doping powders H2 and H3 densify at a low temperature (below 900°C).

3.2. Ceramic characteristics

Sintering temperatures, bulk densities, grain sizes and chemical fluctuations of ceramics are reported in Table 2.

For all calcined powders, the additional milling in alcohol increases the ceramic density. A better de-agglomerated state favours the ceramic densification.

The low temperature sintered ceramics H2 and H3 present the same bulk density range as the calcined powders sintered at 1150°C. The hydrothermal process allows the preparation of dense ceramics at lowest temperature.

For all ceramics, the nickel adding induces a grain size increase and an homogenisation of the microstructure. High temperature densified ceramic H1 has a lower grain size than the Ni added ceramics H2 and H3 sintered below 1000°C. These two last compositions exhibit different sintering behaviours. H2 is fully densified at 950°C and has a coarse grain size (above 6 μm); while H3 density is lower after sintering at 950 and 1000°C and H3-1 and H3-2 are fine grained. The hydrothermal route real interest is achieved with the chemical fluctuation results. Except ceramic H2-1 sintered at too low temperature, all hydrothermally processed ceramics are clearly more homogeneous.

In all cases, the sintering step is also a chemical homogenisation stage. But the hydrothermal process allows the synthesis of powders enough reaction to achieve full homogenisation at the lowest sintering temperature.

3.3. Dielectric and piezoelectric properties

Dielectric and piezoelectric properties are reported in Table 3.

Table 2
Densities, grain sizes and chemical fluctuations of ceramics

Powder process	Powder name	Sintering temperature (°C)	Bulk density (% d_{th})	Grain size (μm)	Inhomogeneity Δx
Calcination	C1-A	1150	92.8	3.5±0.5	0.15
	C1-B	1150	96.8	3.3±0.5	0.12
	C1N-A	1150	91.8	8.5±1.5	0.17
	C1N-B	1150	92.2	7.9±0.7	0.11
	C2-A	1000	92	2.0±0.9	0.17
	C2-B	1000	94.3	2.3±0.5	0.12
	C2N-A	850	91	2.9±0.9	0.12
	C2N-B	850	94.5	3.4±0.5	0.13
Hydrothermal	H1	1150	96.7	2.4±0.2	0.06
	H2-1	850	91.2	3.5±0.4	0.10
	H2-2	950	94.6	6.0±1.0	0.07
	H3-1	950	93.1	3.9±0.5	0.07
	H3-2	1000	93.9	4.8±0.8	0.07

Table 3
Dielectric and piezoelectric properties of ceramics

Powder process	Powder name	ε_r	tan δ (%)	k_p	Q_m	d_{33} (pC/N)
Calcination	C1-A	933±13	7±2	0.35±0.05	167±52	307±52
	C1-B	1033±17	3.5±0.8	0.23±0.02	90±10	242±25
	C1N-A	946±48	4.5±0.5	0.37±0.04	40±5	451±56
	C1N-B	1061±9	0.4±0.1	0.51±0.01	1207±134	602±15
	C2-A	771±9	2.2±0.7	0.29±0.05	312±160	127±21
	C2-B	806±10	5.5±0.3	0.28±0.02	301±70	121±19
	C2N-A	894±10	13.5±1.7	0.24±0.03	98±5	119±16
	C2N-B	1104±11	12±0.7	0.29±0.02	68±4	147±3
Hydrothermal	H1	965±95	0.8±0.2	0.27±0.03	206±41	112±22
	H2-1	980±15	0.5±0.1	0.41±0.01	490±30	232±10
	H2-2	1100±40	0.5±0.1	0.50±0.01	1230±45	317±24
	H3-1	1010±10	0.7±0.2	0.35±0.06	1194±170	188±39
	H3-2	1115±10	0.4±0.1	0.51±0.02	1280±20	310±15

For the calcined route ceramics, the best results are obtained for the alcohol milling composition C1N-B ($Q_m \approx 1200$, $k_p \approx 0.5$, $d_{33} \approx 600$ pC/N, tan $\delta < 0.5$).

The influent parameter seems to be the ceramic grain size depending on the nickel adding and the chemical fluctuation. C1N-A and C1N-B ceramics have the same density and the same grain size order but C1N-B properties are clearly better. The difference is probably due to a better chemical homogeneity and a more homogeneous microstructure for the C1N-B ceramic.

For the hydrothermal route ceramics, the dielectric and piezoelectric properties are once more ameliorated with nickel doping. The best results ($\varepsilon_r \approx 1100$, tan $\delta \approx$ 0,5 $k_p > 0.5$ $Q_m > 1200$ and $d_{33} > 300$ pC/N) are observed for H2-2 and H3-2 ceramics, which are the most homogeneous and the most coarse grained ($5 < \Phi < 6$ μm) hydrothermal ceramics. These results are comparable with the best ones obtained by the classical powder process calcination except for d_{33}. This piezoelectric response decreasing can be explain by the finest grained microstructure[12–14] of the hydrothermal ceramics.

4. Conclusion

Two different routes have been tested to produce homogeneous and dense doped PZT ceramics at lower temperature. A classical calcination way with a lead excess amount to provide a transient liquid phase sintering mechanism and a new hydrothermal powder process which allows the synthesis of homogeneous and reactive powders were investigated.

For the calcination route, the best results are obtained with a nickel doping and the additional milling step. But this powder sinters at high temperature (1150°C). The excess of lead amount in calcined powders decrease significantly the sintering temperature but decreases the resultant piezoelectric properties.

For the hydrothermal route, chemical fluctuations prove the interest of this powder preparation process. Dense and chemically homogeneous ceramics are obtained at low temperatures (950–1000°C) and they have comparable dielectric and piezoelectric properties with the best ceramics prepared by the conventional way. These first results are promising for production of high piezoelectric properties ceramic at low sintering temperature by an hydrothermal route.

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