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Journal of the European Ceramic Society 25 (2005) 2491–2494

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Preparation and characterisation of $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ ceramics
Modelling the device

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Abstract

Ceramics with composition of $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ prepared from powders obtained by hydrothermal synthesis method were investigated. A microstructure with mean grains sizes of 1–3 μm were found and the apparent density of 7.5–7.6 g/cm^3. Dielectric constant and losses have been measured in the range of temperatures (30, 500 °C) with a heating/cooling rate of 0.5 °C/min at frequencies (0.1 Hz, 1 MHz), using impedance spectroscopy method. The transition heat was measured on the small ceramic samples with a differential scanning calorimeter. The permittivity was analysed with phenomenological models for relaxors. Dielectric and piezoelectric constants measured values were used as starting parameters to generate a model of a PZT actuator with ANSYS software package. The model geometry can be modified, after the simulation is performed, in order to achieve the functional objective.

Keywords: Powders-chemical preparation; Nanocomposites; Ferroelectric properties; PZT; Actuators

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1. Introduction

Lead zirconate titanates (PZT) exhibit excellent electromechanical properties and are widely used as ultrasonic resonators, ceramic filters, high-power transducers, actuators.[1] It is well known that these characteristic properties are strongly related to the microstructure of the ceramics; the homogeneity of the raw materials is also important.[2,3] A good-quality piezoceramic material is defined by a high anisotropy degree, which implies a small value of the dielectric constant ε, small dielectric losses, high piezoelectric constants, a relatively high Curie temperature, a raised mechanical quality factor (Q_m), a large anisotropic ratio K_t/K_p (k_t, the thickness coupling factor and k_p, planar coupling factor), high thermal stability of the dielectric and piezoelectric parameters, large frequency constant and increased mechanical strength. There are several ways to approach this matter namely: improvement of the PZT-based ceramics by either compositional modification using various additives, or by using non-conventional technologies (co-precipitation, hydrothermal, sol–gel) allowing the preparation of uniform, sub micrometer-sized and highly-reactive powders or development of new piezoelectric ceramic materials with higher anisotropy, such as lead niobate-based ($PbNb_2O_6$) or bismuth-based composites. Piezoelectric PZT ceramics having the composition at the morphotropic phase boundary (MPB) can be doped with ions to form “hard” and “soft” PZT’s. Hard PZT’s are doped with acceptor ions such as K^+, Na^+ (for A site) and Fe^{3+}, Al^{3+}, Mn^{3+} (for B site), creating oxygen vacancies in the lattice.[4,5] Soft PZT’s are doped with donor ions such as La^{3+} (for A site) and Nb^{5+}, Sb^{5+} (for B site) leading to the creation of A site vacancies in the lattice. The soft PZT’s normally have a higher permittivity, larger losses, higher piezoelectric coefficient and are easy to pole and depole. They can be used

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doi:10.1016/j.jeurceramsoc.2005.03.088

for applications requiring very high piezoelectric properties.

Hydrothermal synthesis is a technology for crystallising materials (chemical compounds) directly from aqueous solutions by adequate control of thermodynamic properties (temperature, pressure and composition).[6] Hydrothermal synthesis offers many advantages over conventional and non-conventional ceramic synthesis methods. All forms of ceramics can be prepared with hydrothermal synthesis namely powders, fibbers, single crystals, coatings on metals, polymers and ceramics.[6] The costs for instrumentation, energy and precursors are far less for hydrothermal methods. Different lead zirconate titanate compositions were synthesized by hydrothermal procedure.[7–12] The aim of the paper is to investigate ceramics with composition of $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ prepared from powders obtained by hydrothermal synthesis method. Dielectric and piezoelectric constants measured values were used as starting parameters to predict a possible application of the niobium doped PZT hydrothermal synthesised as sensor or as an actuator with ANSYS software package.

2. Experimental procedure

Zr(IV), Ti(IV), Pb(II) and Nb(V) aqueous solutions were used as starting materials for niobium doped lead zirconate titanate. These solutions were mixed with an appropriate amount of mineraliser reagent (KOH). Powders based on $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ were then precipitated in Teflon autoclaves (temperature 200 °C, pressure 4.5 bar, time 6 h, at very alkaline pH values), according to the procedure described in Ref. [13]. Powders with large specific area ($S_{BET} = 130\ m^2/g$, picnometric density = $6.59\ g/cm^3$) thus obtained were bounded with 2 wt.% polyvinyl alcohol, granulated and pressed at 1176 MPa. Green pellets (11 mm in diameter and 1.5 mm thick) were sintered 2 h in lead oxide rich atmosphere, at 1150 °C and a heating rate of 3 °C/min, in a CARBOLITE RHF 17/3 furnace. Density of green and sintered pellets was measured using the standard Archimedes method. Chemical quantitative analysis (inductively coupled plasma, ICP; direct coupled plasma, DCP; atomic absorption spectroscopy, AAS) and microstructural investigations (XRD, SEM/EDAX) were performed to characterise PZT powders and sintered products. The dark yellow coloured sintered pellets were lapped to make the surface flat and parallel. Silver paste was applied to both flat surfaces to get metal electrodes. Dielectric constant and losses have been measured in the temperatures range of (30, 500 °C) with a heating/cooling rate of 0.5 °C/min at frequencies (0.1 Hz, 1 MHz), using impedance spectroscopy method (FRA, Solartron SI1260). The transition heat was measured on the small ceramic sintered samples with a differential scanning calorimeter (DSC, Mettler Toledo). A model of a possible application of $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ hydrothermal synthesised using ANSYS software package was generated based on dielectric and piezoelectric measured values.

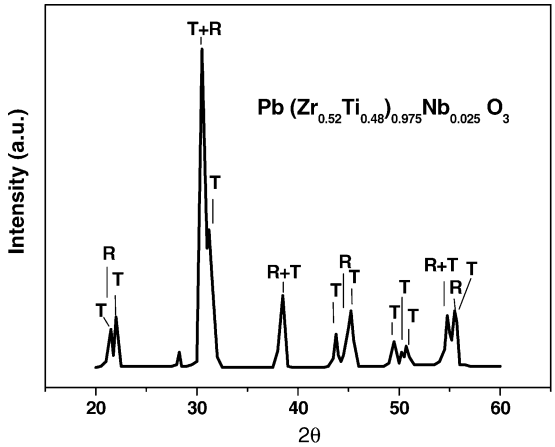

Fig. 1. XRD pattern of PZT-based sintered pellets obtained from powders synthesised in hydrothermal conditions.

3. Results and discussions

3.1. Characterisation of sintered pellets

XRD spectra of sintered pellets have been performed. The measurements have been done using a Cu Kα radiation in a scattering angle range between 20 and 70°. The XRD analysis performed on sintered samples and the indexing procedure showed the presence of a major tetragonal crystalline phase and a minor rhombohedral phase (Fig. 1). The composition of the morphotropic phase boundary (MPB) moves towards the tetragonal phase field according to literature data.[14] Calculated mean crystallite sizes using the half-broadening procedure and Scherrer equation were around 80 nm.

SEM photograph and EDX analysis of the sintered samples after acid etching attack are presented in Fig. 2. The SEM photograph (Fig. 2a) revealed particles with well defined grain boundaries (grain sizes in the range 0.6–3 μm) and columnar structure. EDX analysis (Fig. 2b) indicates that sintered pellets are composed of Pb, Zr, Ti and Nb. Niobium's incorporation seems to be effective.

3.2. Dielectric and calorimetric data

Dielectric constant for all the samples is around 1000 at room temperature and about 15,000–30,000 at the transition temperature. The losses have the following values: at room temperature, $\tan\delta \approx 0.04$ and $\tan\delta \leq 0.2$ in the whole range of temperature (30, 500 °C), for all the investigated frequencies. The Nb-doped PZT show typical relaxor character, with a high dielectric constant, diffuse phase transition and a small dispersion in frequency in the range (1 Hz, 1 MHz), as presented in Fig. 3a, for the sample 2% Nb-PZT. For this composition, the ferro–para phase transition at $f = 1$ Hz is

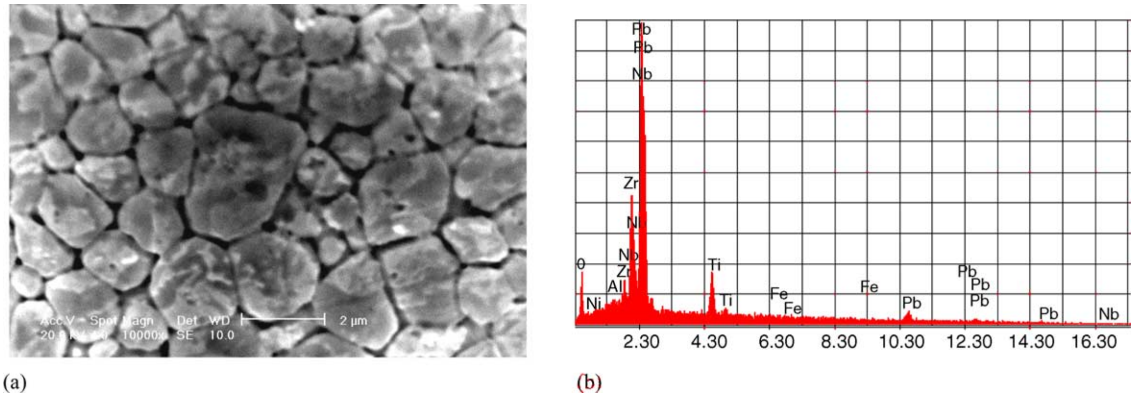

Fig. 2. SEM micrograph (a) and EDX analysis (b) of PZT-based sintered pellets obtained from powders synthesised in hydrothermal conditions after acid etching attack.

around $T_c = 390\,^\circ C$, with a small thermal hysteresis at the heating/cooling cycle of 2 °C. An indication about the relaxor character of this sample is obtained in literature by fitting the dielectric data in the paraelectric phase with empirical laws (modified Curie-Weiss laws). We used the formula proposed in Ref. [15]:

$$\varepsilon = \frac{\varepsilon_m}{1 + (T - T_c/\Delta)^{\gamma}} \qquad (1)$$

in which ε_m is the maximum value of the dielectric constant, T_c the temperature corresponding to this maximum, γ is the diffuseness parameter and Δ indicates the temperature extension of the phase transition, i.e. the Curie region. The diffuseness parameter $\gamma \in [1, 2]$ is describing the Curie-Weiss law when $\gamma = 1$ and the total diffuse phase transition (true relaxor state) if $\gamma \to 2$. These parameters were found by linear fit of the log–log plot $\log(E) = f(\log(T - T_m))$, where:

$$\log(E) = \gamma \log(T - T_m) + \gamma\ \log(\Delta), \quad \text{where} \quad E = \frac{\varepsilon_m}{\varepsilon - 1} \qquad (2)$$

and the fitting results are presented in Fig. 3b. In case of 2% Nb-PZT at $f = 1$ Hz, $\gamma = 1.53$ and $\Delta = 20$ K indicate a mixed character relaxor-ferroelectric. It is interesting to note another anomaly (small shoulder) of $\varepsilon(T)$ around 370 °C (Fig. 4). A careful investigation of the transition heat in the range of temperatures (350, 400 °C) demonstrated the existence of clear maximum at the temperature $T_{st} = 370\,^\circ C$, which is a prove of a structural phase transition which requires a

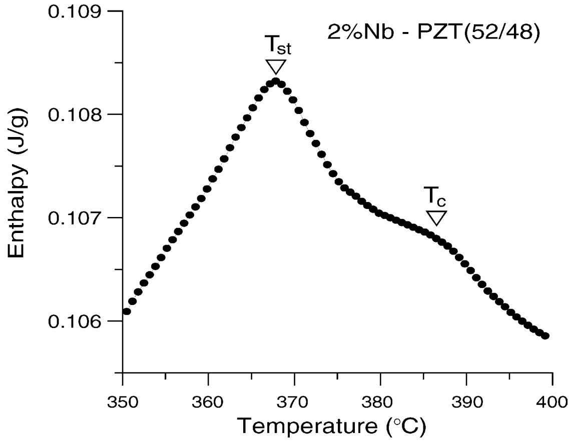

Fig. 4. DSC for PZT-based sintered samples.

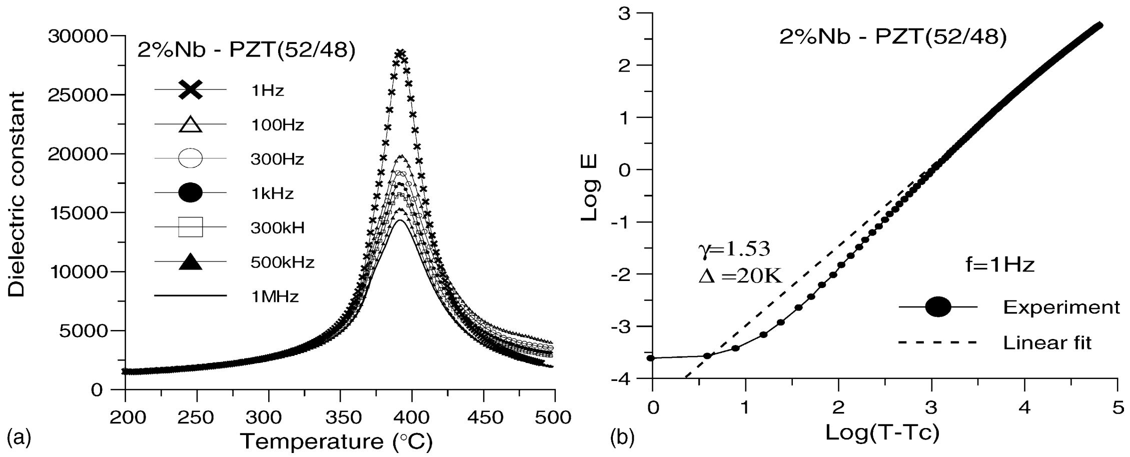

Fig. 3. Dielectric constant as a function of temperature and frequency for PZT-based sintered pellets (a) and fitting results of dielectric constant data (b).

Table 1
Piezoelectric characteristics

Sample	Frequency (Hz)	F_r (kHz)	F_a (kHz)	k_p
0.02Nb-0.98PZT (52/48)	100	214.5	222	0.29

transition enthalpy even higher than those of the phase transition relaxor-paraelectric (detected as a small anomaly in the range 380–400 °C in the DSC data, Fig. 4).

3.3. Piezoelectric characteristics

Polarisation was performed in a silicon oil bath at 100 °C, at 2 kV/mm with a dwell time of 30 min. After 24 h from polarisation the piezoelectric properties were measured. Polarisation degree evaluation was performed by resonance and anti-resonance frequencies measurements and then electromechanical coupling coefficient was calculated. The results are presented in Table 1.

4. Modelling the device

Dielectric and piezoelectric constants measured values were used as starting parameters to generate a model of a PZT surface acoustic device using ANSYS software package. The model geometry can be modified, after the simulation is performed, in order to achieve the functional objective. A possible application domain could be sensors and actuators at very high electric field.

5. Conclusions

The application field of piezoelectric ceramics depends on ceramic material properties, design and function of the device. Ceramic properties can be improved by using new synthesis methods allowing the obtaining of nanostructured powders with improved surface characteristic and enhanced reactivity. Comparing with conventional routes hydrothermal synthesis allows powders grain sizes prediction and controlling.[16] $Pb(Zr_{0.52}Ti_{0.48})_{0.975}Nb_{0.025}O_3$ powders with large specific area ($S_{BET} = 130\,m^2/g$, picnometric density = $6.59\,g/cm^3$) and lower sintering temperature were obtained by hydrothermal procedure and were processed to obtain sintered pellets. A transformation from the normal domain structure to tweed-like structure and nanopolar relaxor short range ordering is also expected by addition of Nb in the composition of PZT. This is proved by the observed mixed character relaxor-ferroelectric (at $f = 1$ Hz, $\gamma = 1.53$ and $\Delta = 20$ K). T_c is higher (400 °C) comparing to a soft PZT type 200 ($T_c = 300$ °C).[17] It is argued that high T_c materials are likely to be more stable for integrated devices then with T_c similar or lower than PZT.[18] Further investigations (piezo, pyro) and $P(E)$ loops can bring new information about the properties of hydrothermal synthesised niobium doped PZT.

Acknowledgements

Romanian Ministry for Education and Research in the frame of National Programme for New Materials, Micro and Nanotechnology and Polar Electro ceramics Network (POLECER) financed by European Community supported the work. The authors thank to dr.Barbara Malic (IJS-Slovenia) for useful discussions and to physicist Jana Pintea (ICPE CA, Romania) for piezoelectric properties measurements.

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