Title: Dielectric and piezoelectric properties of PZT type ceramics obtained by the sol-gel method

Author: Monika Dukat, Aldona Zarycka

Citation style: Dukat Monika, Zarycka Aldona. (2007). Dielectric and piezoelectric properties of PZT type ceramics obtained by the sol-gel method. "Archives of Acoustics" (Vol. 32, no. 4(S) (2007) s. 65-70).

ARCHIVES OF ACOUSTICS
32, 4 (Supplement), 65–70 (2007)

DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF PZT TYPE CERAMICS OBTAINED BY THE SOL-GEL METHOD

Monika DUKAT, Aldona ZARYCKA

University of Silesia
Faculty of Computers Science and Materials Science
Żeromskiego 3, 41-200 Sosnowiec, Poland
e-mail: monika_dukat@spi.net.pl

(*received July 15, 2007; accepted October 5, 2007*)

A sol-gel method belongs to chemical methods of producing non-organic and non-metallic materials. As a result of a synthesis by the sol-gel method a powder with the $\mathrm{Pb(Zr_{0.35}Ti_{0.65})O_3}$ chemical composition, which was formed and sintered freely, and hot pressed as well, was obtained. The obtained ceramic material was subjected to test of properties of permittivity, loss tangent and piezoelectric properties as well. Both a description of a technological process to obtain ceramic materials by the sol-gel method and the determined dielectric and piezoelectric parameters of the ceramic in question are presented in this work. The ceramic in question can be used, among others, in pressure sensors, electroacoustic transducers, piezoceramic amplifiers, loudspeakers and microphones.

Keywords: sol-gel method, PZT ceramic, permittivity, dielectric losses.

1. Introduction

The $\mathrm{PbZrO_3}$ and $\mathrm{PbTiO_3}$ solid solution with a general molecular formula of $\mathrm{Pb(Zr_x Ti_{1-x})O_3}$ constitutes a PZT ceramic material. The PZT ceramic shows a crystalline structure of a perovskite type. The ideal perovskite is $\mathrm{CaTiO_3}$ calcium titanate, a rare mineral with dielectric properties, with a regular structure Pm3m, crystallizing at high temperature and elevated pressure [1–3].

The sol-gel method is a process of obtaining ceramic materials based on a transition from a liquid sol system (usually colloidal) into a solid gel phase. This method enables to produce a ceramic in different forms e.g.: thin layers, fibers, and a solid ceramic. The sol-gel method was developed in the mid fifties of the XX-th century in connection with replacing fuel metallic elements in nuclear reactors by oxide elements. The sol-gel synthesis of ceramic powders supersedes gradually a conventional method of their obtaining, based on a synthesis of simple oxide mixtures as a result of high temperature sintering. High purity and homogeneity of fundamental materials used have a significant influence on properties of products. Materials obtained by the sol-gel method are characterized by better chemical purity and high density of materials after sintering. This method also enables to obtain a ceramic with compositions, which cannot be obtained as result of a synthesis process by a reaction in the solid phase of simple oxides and showing specific physical-chemical properties. Dielectric and piezoelectric properties of the PZT ceramic depend mainly on the solid solution composition, its chemical homogeneity, a microstructure and on a production technology [4–6].

An aim of this work was to obtain a PZT ceramic material with the $Pb(Zr_{0.35}Ti_{0.65})O_3$ composition by the sol-gel method and to examine dielectric and piezoelectric properties of specimens compacted by a free sintering and hot pressing method.

2. Experimental procedure

A solid solution of the PZT type with the $Pb(Zr_{0.35}Ti_{0.65})O_3$, molecular formula, where the Zr/Ti ratio is 35/65, characterized by a tetragonal structure, was the material subjected to tests. The PZT ceramic material was obtained by the sol-gel technology by a synthesis reaction of organic metal salts in the liquid phase. In order to obtain a ceramic material the following precursors were used: lead acetate, zirconium propanolan, titanium propanolan, propanol and acetylacetone. A synthesis process of the PZT material lasted 45 min., the obtained product was subjected to distillation, during which a by product ester-propyl acetate was removed. After the distillation the acetylacetone and distilled water were added. Hydrolyze reactions resulted in sol formation, and then gel. After drying of the liquid phase xerogel was obtained and it was subjected to roasting at 873 K for 2 hours to burn up organic compounds. The PZT ceramic material obtained was ground for 2 hours. Then, it was formed into tablets of 10 mm diameter, followed by free sintering at the temperature of 1573 K for 5 h, and they were also subjected to hot pressing at the temperature of 1400 K under the pressure of 20 MPa for 2 hours. The obtained specimens of 1 mm thickness were covered with silver paste electrodes by burning for 5 h at 1073 K temperature. The obtained specimens were subjected to tests of dielectric and piezoelectric properties. In order to determine the microstructure characteristic of the ceramic material obtained, examinations were made by use of a scanning electron microscope. Permittivity and tangent loss were examined by a bridge of a BM 595 type. This bridge controlled by microprocessor enabled to read out a value of capacitance C, which was next used for ε permittivity calculations. Changes in C capacitance and loss tangent in a temperature function and frequency of a measurement field while heating and cooling the specimens were examined. The tests were performed in the sinusoidal changeable field with frequency from 100 Hz to 20 kHz in a temperature range from 295 K to 750 K. In order to examine piezoelectric properties the PZT ceramic was subjected to an influence of constant electrical field, namely the ceramic material was polarized. The following polarization conditions were assumed: intensity of polarization field 20 kV/cm, polarization temperature 400 K, duration of polarization process 2 h. Piezoelectric parameters were determined by resonance and antiresonance method [7, 8].

3. Investigation results

Examples of temperature dependences of permittivity $\varepsilon(T)$ and loss tangent $\tan\delta(T)$ for the PZT ceramic compacted by free sintering method and hot pressing are presented in Figs. 1 and 2. The $\varepsilon(T)$ curves show characteristic maxima in the phase transition area. The initial ε value increases with increasing temperature reaching the maximum value ε_m at the phase transition temperature T_c. The further increase in the temperature results in a decrease in the ε value above the Curie temperature, in accordance with the Curie–Weiss law.

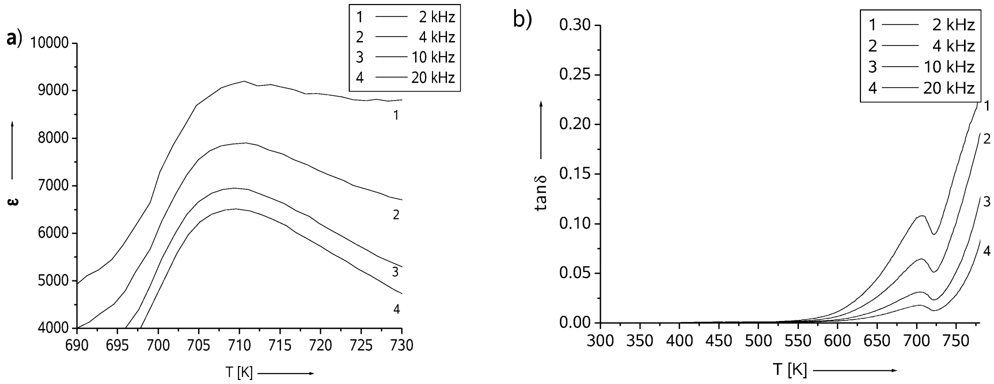

Fig. 1. Temperature dependences obtained for the PZT ceramic 35/65 compacted by a free sintering method: a) permittivity – $\varepsilon(T)$, b) loss tangent – $\tan\delta(T)$.

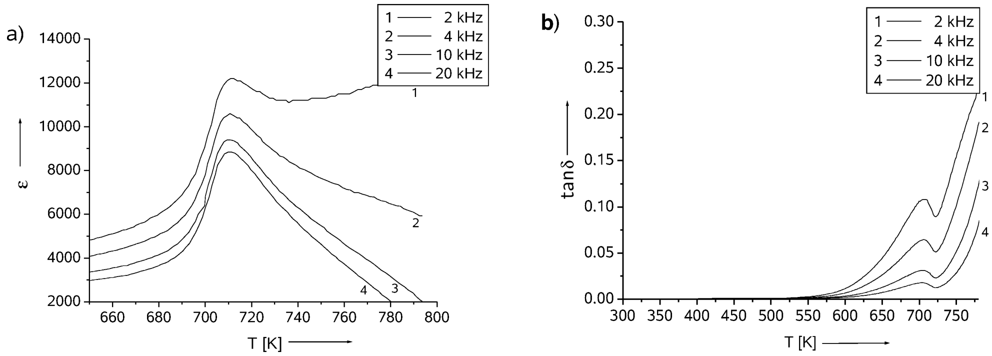

Fig. 2. Temperature dependences obtained for the PZT ceramic 35/65 compacted by a hot pressing method: a) permittivity $\varepsilon(T)$, b) loss tangent – $\tan\delta(T)$.

Low values of dielectric loss angle in the temperature range of 295–600 K being approximately 0.01 prove high quality of the material obtained. For both compacting methods, a decrease in the loss tangent value with an increase in frequency is observed (Fig. 1, 2).

The $\tan\delta$ value at T_c temperature for the PZT 35/65 specimens in question for the measurement field of 2 kHz frequency did not exceed a unit. At comparable $\tan\delta$ values for a specimen compacted by a hot pressing method higher values of permittivity were obtained both at room temperature and at the Curie temperature.

Density of the ceramic specimens obtained by a hot pressing method is 7515 kg/m^3, whereas density of the specimen obtained by free sintering methods is 5432 kg/m^3. It has been found that the ceramic compacted by a hot pressing method is characterized by higher density than the ceramic compacted by a classical method, because the pressing method that is sintering under pressure ensures greater conformity of stoichiometry of the synthesized components of the obtained ceramic. An advantage of this method is a possibility to sinter compacts in a small tightly locked chamber, what prevents volatilization of components. It also enables to lower a temperature of sintering and to reduce sintering time. The external pressure, exerted on the prepared compact while sintering, brings powder grains closer and it increases an area of the mutual contact and removes pores. It enables to obtain a non-porous and fine-grained ceramic what has a significant influence on dielectric and piezoelectric properties.

Crystalline ceramic materials have a polycrystalline structure. Each grain is a less or more perfect crystal with inter-grain boundaries contacting the adjacent crystals. The PZT ceramic is a polycrystalline sinter, characterized by high cohesion and strength. It is a multiphase system in which three phases can be distinguished: crystalline consisting of crystallite of a given solid solution or a chemical compound, glasslike phase (an amorphous layer binding other phases), a gaseous phase filling ceramic pores. For the PZT 35/65 ceramic composition in question microphotographs presented in Fig. 3 were taken and they illustrate the microstructure and domain structure of the non-polarized PZT ceramic compacted by a hot pressing method.

The ceramic microstructure depends on many factors. Among others on a technological process, types of fundamental materials, kinetics of phases transitions, sintering time, grain growth conditions. Well-formed grains and boundaries between grains, being 120°, were observed. The PZT 35/65 ferroelectric ceramic in the tetragonal phase

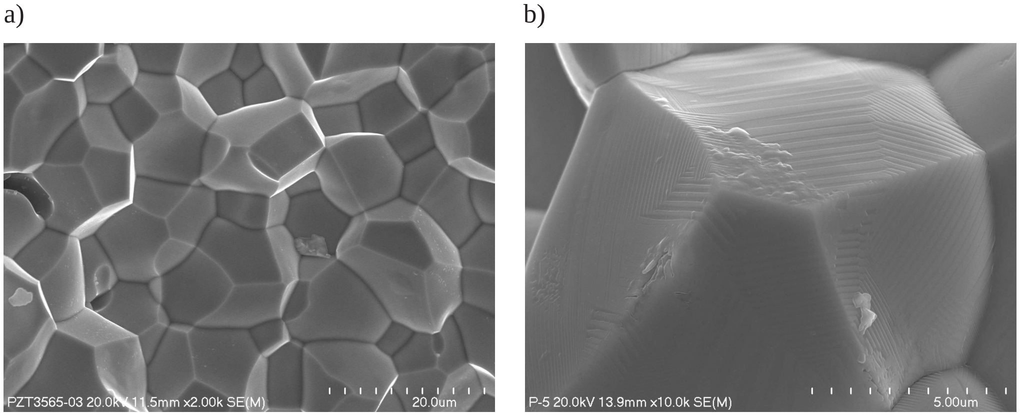

Fig. 3. Micro-photographs (SEM) of the PZT 35/65 ceramic: a) microstructure, b) domain structure.

is characterized by high concentration of 90° structural domains (Fig. 3). Piezoelectric parameters for the PZT ceramic composition in question were determined by resonance and antiresonance method, reading values of frequency f resonance, antiresonance and first overtone. On basis of the obtained values piezoelectric parameters of the polarized PZT ceramic compacted by a hot pressing method were calculated. Values of parameters of the PZT 35/65 ceramic are presented in Table 1. Comparing properties of the obtained PZT 35/65 ceramic with a multicomponent piezoceramic with the composition of $Pb_{0.94}Sr_{0.06}(Zr_{0.5}Ti_{0.5})O_3$ + 0.25% wt. Cr_2O_3 and also $(x)PbTiO_3-(1-x-y)PbZrO_3-y[Pb(Cd_{0.5}W_{0.5})O_3]$, where $x=0.65$, $y=0.02$ obtained by a free sintering method, better parameters for the ceramic examined in this work were observed; parameters such as e.g. a value of electromechanical coefficient k_p for the composition in question was 0.41, sound speed $V_R = 2755$ m/s, whereas for the multicomponent composition $Pb_{0.94}Sr_{0.06}(Zr_{0.5}Ti_{0.5})O_3$ + 0.25% wt. Cr_2O_3 k_p was 0.35, $V_R = 2150$ m/s, whereas for $(x)PbTiO_3-(1-x-y)PbZrO_3-y[Pb(Cd_{0.5}W_{0.5})O_3]$ where $x = 0.65$, $y = 0.02$ a value of the electromechanical coefficient was 0.38, and sound speed was 2204 m/s, what means that the obtained material can be used successfully in ultrasound transducers [9–11].

Table 1. Values of piezoelectric parameters determined for the PZT 35/65 ceramic.

Parameter	Values
Poisson's ratio	0.38
Electromechanical coupling coefficient k_p	0.41
Transverse electromechanical coupling coefficient k_{31}	0.22
Piezoelectric module $d_{31} \cdot 10^{12}$ [C/N]	36.6
Sound speed V_R [m/s]	2755
Elastic susceptibility $S_{11}^E \cdot 10^{11}$ [m^2/N]	1.08
Elastic susceptibility $S_{12}^E \cdot 10^{12}$ [N/m^2]	−4.21
Coefficient of elasticity $C_{11}^E \cdot 10^{10}$ [N/m^2]	9.22
Coefficient $g_{11} \cdot 10^3$ [Vm/N]	15.18

4. Recapitulation

Examinations of properties of a solid solution of $Pb(Zr_{1-x}Ti_x)O_3$ type allow to determine dielectric and piezoelectric parameters in a detailed way and possibilities of their application in many fields of life and industry branches in electronic engineering, micro-electronic engineering, radio engineering, optical electronic engineering and also in medicine). A ceramic combining different types of optimum properties: dielectric, mechanical, piezoelectric, optical, and important for applications in various equipment such as: pressure sensors electroacoustic transducers, condensers, servomotors, FRAM memory, piezoceramic amplifiers, loudspeakers, microphones, piezoceramic gas lighters, is of great interest. In this work a production method of the PZT 35/65 ceramic as a result of the sol-gel synthesis was described, and results of experimental tests are also presented.

It has been shown that an application of the sol-gel the technology to synthesize ceramic powders improves piezoelectric and dielectric parameters of the ceramic specimens in question. Densification of the $\mathrm{Pb(Zr_{0.35}Ti_{0.65})O_3}$ ceramic powder in the hot pressing process, because of higher pressure and temperature of sintering enables to obtain a material with higher k_p and d_{31} values (Table 1).

References

[1] SZYMAŃSKI A., *Mineralologia techniczna*, Wydawnictwo Naukowe PWN, Warszawa 1997.

[2] SUROWIAK Z., *Tworzywa ceramiczne o strukturze typu perowskitu jako materiały dla elektroniki*, Ceramika, Polski Biuletyn Ceramiczny, **80**, 39–50 (2003).

[3] BOCHENEK D., FESENKO E. G., GAVRILYACHENKO V. G., *Piezoelektryczne rezonatory na bazie PZT*, [w:] *Elektroceramika ferroelektryczna*, SUROWIAK Z. [red.], Wydawnictwo Uniwersytetu Śląskiego, Katowice 2004.

[4] PŁOŃSKA M., CZEKAJ D., SUROWIAK Z., *Zastosowanie metody zolowo-żelowej w technologii ceramicznych nanoproszków ferroelektrycznych 8/65/35 PLZT*, Ceramika, Polski Biuletyn Ceramiczny, **66**, 594–601 (2001).

[5] OSIŃSKA K., *Struktura i właściwości fizyczne ceramiki i cienkich warstw ferroelektrycznych PZT, otrzymanych metodą zolowo–żelową*, [w:] Prace Wydziału Techniki 30, Ferroelektryki tlenowo-oktaedryczne, Wydawnicwo Uniwersytetu Śląskiego, Katowice 1997.

[6] OCZOŚ K. E., *Kształtowanie ceramicznych materiałów technicznych*, Oficyna Wydawnicza Politechniki Rzeszowskiej, Rzeszów 1996.

[7] BRUŚ B., ILCZUK J., ZARYCKA A., CZERWIEC M., *Wpływ technologii otrzymywania na właściwości dielektryczne ceramiki typu PZT*, Ceramika, Polski Biuletyn Ceramiczny, **80**, 493–498 (2003).

[8] ILCZUK J., ZARYCKA A., CZERWIEC M., *Synteza i właściwości piezoelektryczne ceramiki typu PZT otrzymanej metodą zolowo–żelową*, Ceramika, Polski Biuletyn Ceramiczny, **89**, 116–121 (2005).

[9] ZACHARIASZ R., CZERWIEC M., *Praktyczne zastosowania ferroelektrycznej ceramiki typu PZT*, Materiały 52 Otwartego Seminarium z Akustyki, Polskie Towarzystwo Akustyczne – Oddział Poznański, pp. 211–214, Poznań – Wągrowiec 2005.

[10] ZARYCKA A., BRUŚ B., ILCZUK J., CZERWIEC M., DUKAT M., *The internal friction background In the PZT ceramics obtained by the sol-gel method*, Materials Science – Poland, 2007 [in press].

[11] BRUŚ B., ZARYCKA A., CZERWIEC M., ILCZUK J., *Relationship between obtaining method and piezoelectric properties of the PZT type ceramic*, Molecular and Quantum Acustics, **27**, 63–70 (2006); *ol*, pp. 293–298 (1988).