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SYNTHESIS AND PROPERTIES
OF NANOSTRUCTURED PZT PIEZOCERAMICS

V.V. Prisedsky, V.M.Pogibko*
Donetsk National Technical University,
*Scientific and technological center "Reaktivelektron"

Образцы пьезокерамики цирконата-титаната свинца (ЦТС) получены спеканием нанопорошка $Pb(Zr_{0,52}Ti_{0,48})O_3$, синтезированного термолизом оксалатного прекурсора. Наноструктурная керамика ЦТС спекается при более низких температурах и имеет более высокие (на 25 - 45 %) электрофизические свойства по сравнению с образцами по традиционной технологии.

Due to their superior electrophysical properties, lead zirconate–titanate (PZT) solid solutions remain for decades the most widely used piezoelectric ceramic materials. During the last decades, the potential of increasing the properties by the synthesis of nanocrystalline PZT powders and consolidated nanostructured ceramics attracts increasing interest of researchers [1].

The size dependences of most physical and chemical properties are stronger in the nanometer range than those for larger, micro- and macroparticles. The Curie temperature T_C of nanopowder $BaTiO_3$ decreases with decreasing particle size indicating the suppression of ferroelectric state. A fundamental technological advantage of nanocrystalline PZT powders is better sintering at reduced temperatures as compared to the conventional solid-state process.

In the present paper, we report the synthesis and properties of bulk nanostructured $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics consolidated by compaction and sintering of nanocrystalline PZT powder (d_{av} = 25 nm) obtained from an oxalate precursor.

Reagent grade titanium tetrachloride $TiCl_4$, zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$, lead nitrate $Pb(NO_3)_2$, oxalic acid $H_2C_2O_4 \cdot 2H_2O$, ammonia NH_3 25% water solution and bidistilled water were used as starting materials to precipitate a PZT oxalate precursor. Based on preliminary study of kinetics of the process we used the following procedure of synthesis of nanocrystalline PZT.

Powder sample of oxalate precursor was distributed in thin (≤ 4 mm) layer in alundum crucible and placed into an oven with silicon carbide heaters, then heated to 370 °C at 15 °C/min and dwelled at this temperature

for 45 min. After that it was heated quickly to 750 °C passing a high-gradient temperature field and kept at maximum temperature of 750 °C for 45 min and cooled with the oven.

Phase composition and average crystallite size in studied samples were determined by X-ray powder diffraction analysis. X-ray diffraction data were collected on DRON-3 diffractometer using Ni-filtered Cu K_α radiation at scanning rates 2°(2θ)/min. Morphology and dimensions of grains in powdered and ceramic samples were studied by transmission (JEM 200A, JEOL) and scanning (TSM T30, JEOL) electron microscopy. Surface area was measured by Brunauer–Emmet–Teller (BET) method (Soft-Sorbi–II). Shrinkage curves at sintering were recorded with DIL 402 PC dilatometer.

Capacity and dielectric loss were measured at 1 kHz. Piezoelectric properties were measured by resonance-antiresonance method on disk 10 Ч 1 mm specimens at 1 kHz. The specimens were polarized for 30min in polyethylsiloxan at 120-150 °C in the field of 4 kV/mm.

As seen from electron microphotographs (TEM) of synthesized PZT powder (Fig. 1), the particles are uniform with average size d_{av} = 25 nm. Complete formation of PZT solid solution after calcination oxalate precursor at maximum temperature of 750 °C is confirmed by X-ray diffraction analysis. According to XRD, synthesized powder is a single-phased perovskite.
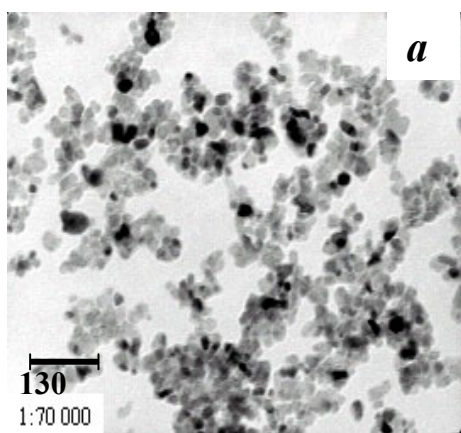

Fig. 1. TEM microphotographs of PZT powder synthesized from oxalate precursor.

Ceramic specimens in the form of disks 10 mm in diameter and 1.0-1.5 mm thick were pressed and then sintered from the synthesized PZT powder. A high degree of dispersion, the uniformity in sizes and an extensive interparticle adhesion create substantial difficulties in forming bulk compacts from nanocrystalline powders.

To obtain satisfactory results at the forming step, we added a liquid surface active (SAS) binder to enhance sliding and rotation of nanocrystallites in a pressed pellet, and also the maximum pressure of forming was increased to 600 MPa.

Fig. 2 shows the results of the dilatometric analysis. The sintering behavior of nanocrystalline PZT powder is compared with that of convention-

ally synthesized microcrystalline PZT. In both cases, a small volumetric expansion is observed before a pronounced densification starts. In the polythermal regime of heating the nanocrystalline sample at the rate of 10 єC/min, the shrinkage starts at 600 єC and is over at 950 єC. This is lower by more than 300 єC than those temperatures for conventionally prepared PZT powder.
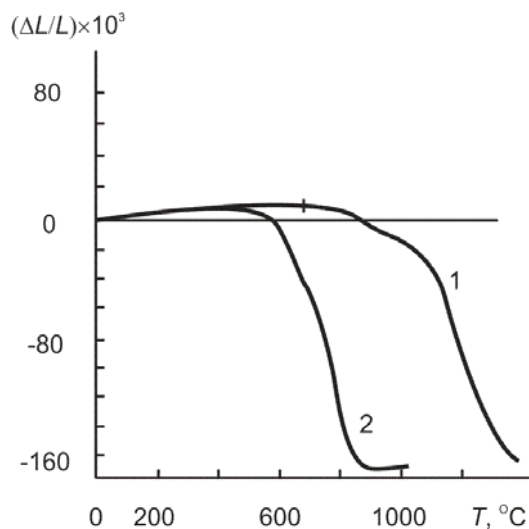

Fig. 2. Dilatometric curves for sintering PZT pressed powders: 1 – conventional solid-state synthesis; 2 – nanocrystalline powder obtained from oxalate precursor. Heating rate: 10 єC/min.

One and half an hour of isothermal sintering at 850 єC is sufficient to decrease the total residual porosity of the specimens below 3 % . This value is characteristic for high-quality PZT ceramics obtained by free sintering. The sintering kinetics shows a semilogarithmic behavior: the decrease in porosity ($и_0 - и$) changes linearly with logarithm time. The semilogarithmic behavior is valid both for intermediate and final stages of sintering and corresponds to the equation (1) proposed by Coble for the densification model of vacancy lattice diffusion from pores to their sinks at the grain boundaries with concurrent grain growth according to the cubic law (2):

$$\Theta_0 - \Theta = B(T)\ln\tau = \frac{N\cdot\sigma\cdot D\cdot a^3}{A\cdot kT}\cdot\ln\tau \tag{1}$$

$$d_g^3 - d_{g(0)}^3 = A(T)\cdot\tau \tag{2}$$

Compaction of nanosized powders offers many ways to decreasing their high surface energy. One of them is sliding and rotation of adjacent nanoparticles until a better adjustment of their crystallographic orientations, thus lowering the grain-boundary energy. This process leads to the formation of much larger grain associations including a great number of initial nanoparticles correlated in the orientation. It is important to note that these larger grains do not appear as a result of normal grain growth of initial nanoparticles but as a consequence of their reorientation and merging. SEM studies show that, in the temperature interval of sintering, these processes occur at a considerable rate and lead to formation and consequent growth of larger submicro- and even micrometer-range grains (Fig. 3).
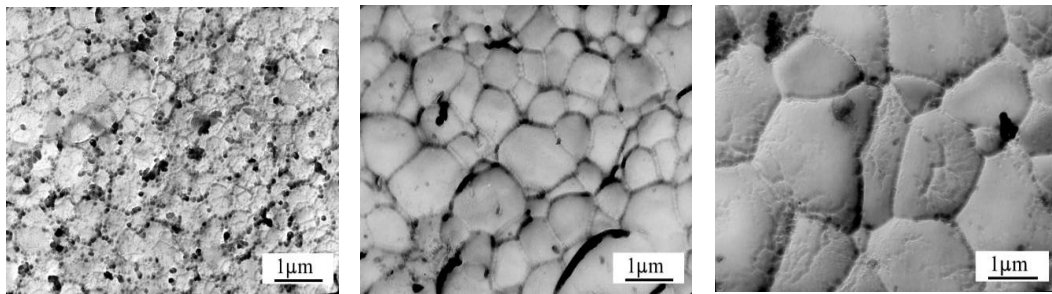
Fig. 3. Formation and growth of microcrystalline grains in the course of
sintering nanocrystalline PZT compacts. Time of treatment at 800 °C,
min: *a* – 30; *b* –60; *c* – 180.

As a result, the microstructure of a sintered specimen includes both
nanosize crystallites (d_c) ascending from initial nanoparticles and also lar-
ger microsize grains (d_g). These larger grains are separated with large-
angle boundaries while the nanocrystallites within them – with low-angle
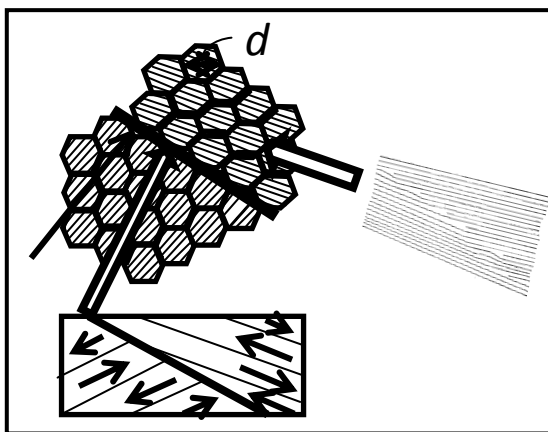ones (Fig. 4). The nanocrystallites
may be determined experimentally
as regions of coherent X-ray scat-
tering (RCS). In fact, the grains
with large-angle boundaries and
RCS may be observed in any
polycrystalline material. The ac-
tual benefit of PZT ceramic mate-
rial consolidated by sintering a
nanocrystalline PZT powder is a
controlled dimension of crystal-
lites (RCS) inside the nanometer
range and, in this way, the assur-
ance of a nanostructured character
of the sintered ceramics.

Fig. 4. A schematic presentation of
low- and high-angle boundaries in
nanostructured ceramics.

As seen in the Table, electro-
physical properties of $Pb(Zr_{0/52}Ti_{0.48})O_3$, piezoceramics consolidated by sin-
tering nanocrystalline powder (nc) are substantially higher than those of
samples sintered by conventional technology (ct). The values of the piezo-
moduli d_{31} and d_{33} (nc) are higher by 25–30 %, the dielectric permettivityt
$ε_{33}/ε_0$ (nc) – by 45 %. The values of the electromechanical coupling factor
K_p, the mechanical quality factor Q_m, the dielectric losses tg δ are also im-
proved for nanostructured samples. High dielectric and piezoelectric prop-
erties of PZT ceramics obtained from nanopowders confirm that the
nanocrystallites within a microcrystalline grain are interconnected – their
low-angle boundaries do not prevent the consolidation of atomic vibrations

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into a joint oscillator ensemble within a ferroelectric domain.

Table

Electrophysical properties of PZT piezoceramics, consolidated from nanocrystalline powder (nc) and conventional technology (ct)

Samples	$\varepsilon_{33}/\varepsilon_0$	tg δ	K_p	Q_m	d_{31}, pC/N	d_{33}, pC/N	T_c, $^\mathrm{e}$C
Pb(Zr$_{0,52}$Ti$_{0,48}$)O$_3$, (nc)	1100 ± 60	0,0030	0,54	650	120 ± 5	270 ±10	385
Pb(Zr$_{0,52}$Ti$_{0,48}$)O$_3$, (ct)	760 ± 70	0,0040	0,52	500	90 ± 7	220 ±15	385
Pb(Zr$_{0,52}$Ti$_{0,48}$)O$_3$ + 0,7% mol. MnO$_2$, (nc)	1250 ± 75	0,0035	0,58	1100	160 ± 8	500 ± 30	385
ЦТССт3 (ct)	1400 ± 90	0,0055	0,55	>800	140 ± 10	295 ± 35	290

In this respect consolidated ceramics is distinguished from free standing particles in a nanopowder, in which a decrease in size produces a reduction in the Curie temperature and suppression of ferroelectric properties. At the same time, local mechanical stresses on developed boundary surfaces of nanocrystallites, in particular at dislocations and disclinations, might cause formation of pseudomorphotropic regions, contributing to enhancement of movements of ferroelectric domain walls, reorientations of the polarization thus increasing corresponding ferroelectric properties. In PZT ceramics consolidated from nanopowders such surfaces are more developed than in specimens sintered by traditional solid-state technology. Quantitative differences in correlation between dimensions of crystallites (RCS) and larger grains separated with large-angle boundaries result in higher dielectric and piezoelectric properties of PZT piezoceramics consolidated by sintering from nanocrystalline powders.

1.   V.V. Prisedskii, V.V. Pogibko, V.S. Polishchuk Production and Properties of Nanostructured Metal-Oxide Lead Zirconate–Titanate Piezoceramics //Powder Metallurgy and Metal Ceramics. – 2014. – V.52, No.9-10. – P.505-513.