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Polyoxidic Thick Films for Piezoelectric Energy Harvesters

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***Abstract* – Thick films of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3–0.35PbTiO_3$ were studied as piezoelectric active elements for micro-electro-mechanical systems for piezoelectric energy harvesting. The best phase purity, dielectric and piezoelectric properties were tested. The piezoelectric coefficient was found equal to 120 pC/N.**

Keywords – polyoxidic thick films, piezoelectric energy harvesters.

I. INTRODUCTION

The technology of thick-film is increasingly used to create simple and robust functional structures. Screen-printing technology is one of the most widely used thick-film deposition techniques (up to 100 micrometres thick uniform films). If speaking about piezoelectric thick films, they are mostly based on e.g. Pb(Zr,Ti)O3 solid solution [1-3], printed on common substrate materials such as silicon or alumina. A more sophisticated recipe of active film is based on (1-x)Pb(Mg1/3Nb2/3)O3–xPbTiO3 (PMN–100xPT) solid solutions, with the morphotropic phase boundary at x = 0.35 [2, 3]. It was shown that PMN–35PT thick films prepared on e.g. silicon substrate possess high dielectric permittivity (at least 3000 at 1 kHz and room temperature [4-6]) and high piezoelectric coefficients (d33 of 150-200 pC/N [6, 7]), so being promising candidates for piezoelectric energy harvesters.

The aim of this work was to examine the compatibility of PMN–35PT piezoelectric thick films with metalized substrates and to test their phase purity, dielectric and piezoelectric properties. It was noticed that the glass phase of ceramic substrate may interact with PMN–35PT [8, 9], which leads to changes in the thick film's phase composition and consequently functional properties. In order to prevent the film-substrate interactions, in this work the PMN–35PT thick films were prepared on metalized substrates (Ag), as interposed 15μm layers.

II. EXPERIMENTAL METHODS

For the synthesis of the PMN–35PT powder next materials were used: PbO (99.9%, Aldrich), MgO (98%, Aldrich), TiO2 (99.8%, Alfa Aesar) and Nb2O5 (99.9%, Aldrich). These oxides were mixed in the molar ratio corresponding to the PMN–35PT stoichiometry with an excess of 2 mol% lead monoxide was high-energy milled for 72 h at 300 rpm, and additionally in a mill for 4 h at 800 rpm in isopropanol. After that the powder was heated at 700 °C for 1 h. The powders were dispersed in acetone under ultrasound, and a few drops were spread on highly oriented pyrolytic graphite substrates. The thick-film paste (PMN–35PT) was prepared from a mixture of the PMN–35PT powder and an organic vehicle consisting of alpha-terpineol, [2-(2-butoxy-ethoxy)-ethyl]-acetate and ethyl cellulose in the ratio 60/25/15, [10].

The PMN–35PT paste was printed up to 3 times on the substrate with intermediate drying at 150 °C. The samples were pressed at 50 MPa, heated at 500 °C for 1 h to decompose the organic vehicle, sintered at 850 °C for 2 h in covered alumina crucibles in the presence of PbZrO3 packing powder having an excess of 2 mol% lead monoxide and after that cooled to room temperature with a rate of 2 °C/min, [10].

Complete analyses as X-ray diffraction (XRD) patterns, FE-SEM micrographs of the films and the energy-dispersive X-ray spectroscopy (EDXS) at 15 keV were performed. For dielectric (dielectric losses - tan δ and permittivity - ε` up to 100 kHz, versus temperature) and related piezoelectric measurements, Cr/Au electrodes with a 1.5-mm diameter were deposited on the top area of the films using RF-magnetron sputtering (5 Pascal). For enhancing the piezoelectric features, the films were poled at 160 °C with a dc electric field from 2.5 to 7.5 kV/mm for 5 min and field-cooled to 25 °C, and the piezoelectric constant d33 was measured.

III. RESULTS AND DISCUSSION

The distribution of the particle size of the PMN–35PT powder used for preparation of the thick-film paste is shown in Fig. 1(a). The d_{50} was 0.32 μm. The majority of particles have a sub-micrometre size, confirmed by the FE-SEM analysis, Figure 1(b). The XRD pattern of PMN–35PT is shown in Fig. 1(c), where all reflections

correspond to the perovskite phase.

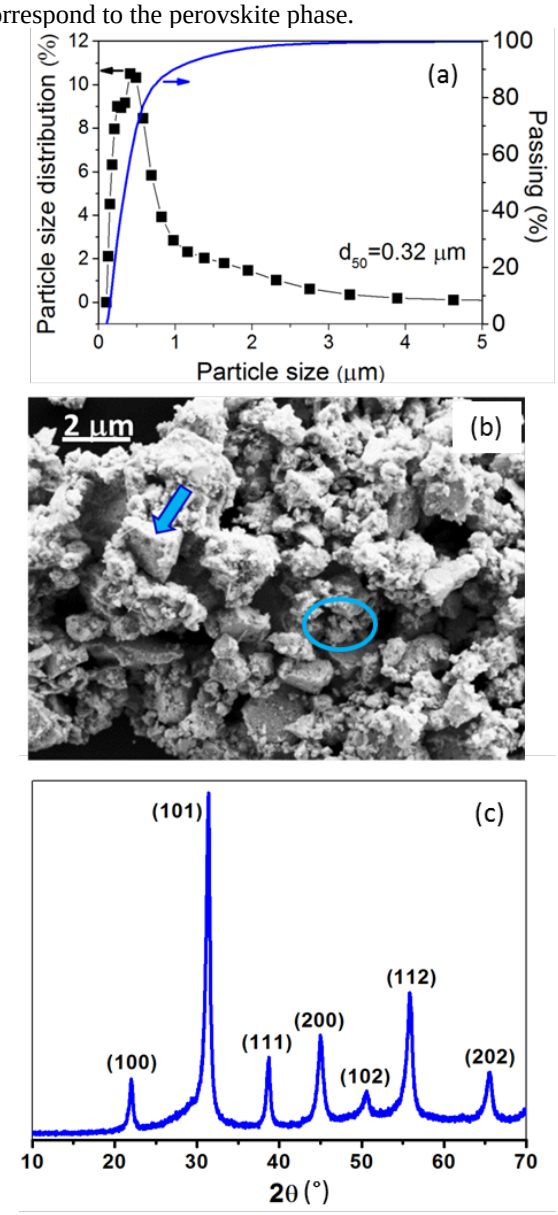

Fig. 1: (a) The particle size distribution, (b) FE-SEM micrograph and (c) XRD pattern of PMN–35PT powder

In Fig. 2 the ε` and tan δ vs. temperature are shown for the PMN–35PT thick film on substrate. At 30 °C and 1 kHz the ε` and tan δ are e.g. 1150 and 0.06, respectively.

The local piezoelectric features were further investigated, and correlated with topography and out-of-plane PFM amplitude images, as shown in Fig. 3 (a) and (b), respectively. In the topographical image, the grain boundaries can be clearly identified, while in the amplitude image the grain boundaries are visible as dark non-active boundaries. The enhanced local piezoelectric activity is evident as brighter areas within the grains, e.g. region no. 1 in Fig. 3 (b). The size of the domains varies from a few hundred nanometres to a micrometre, i.e. marked by arrows in Fig. 3 (b). The local PFM amplitude and phase hysteresis loops are shown in Fig. 3 (c) confirming a typical hysteretic response of the ferroelectric material.

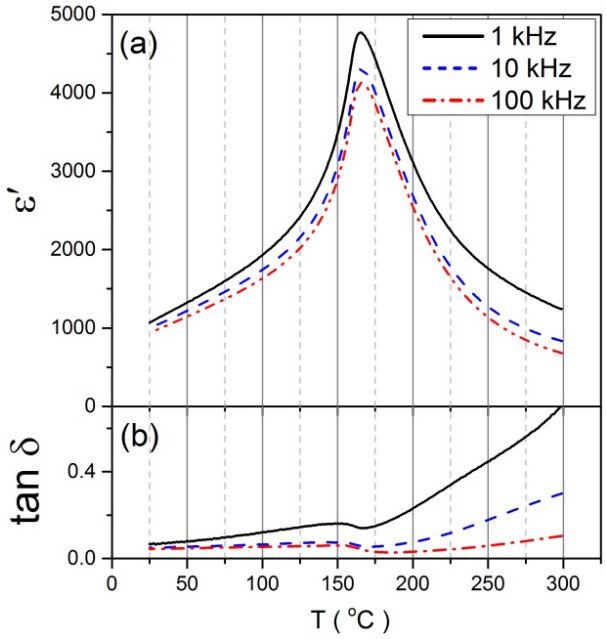

Fig. 2: (a) ε' and (b) tan δ of the PMN–35PT film on gilded substrate as a function of temperature at 1, 10 and 100 kHz

Finally, the d_{33} values are presented in Table 1 for different poling values. The d_{33} increased with the increasing of poling field until 5.5 kV/mm, from where a saturation phenomenon was noticed. The highest value of d_{33} was 120 pC/N, a very convenient value for piezoelectric harvesting applications.

Table 1: The piezoelectric coefficient d_{33} measured for the PMN–35PT films poled at different electric field amplitudes.

E_{poling} (kV/mm)	d_{33} (pC/N)
2.5	65
3.5	85
4.5	100
5.5	120
6.5	120
7.5	120

No degradation of PMN–35PT films due to substrate was noticed.

IV. CONCLUSIONS

The compatibility of piezoelectric PMN–35PT thick-films with metalized ceramic substrates was studied, as a prerequisite for generating stable piezoelectric structures. Up to 100 µm thick PMN–35PT films on Ag-metalized substrate were produced, where no film-substrate interactions was noticed.

The XRD analysis revealed the existence of a large

quantity of secondary phases in the films prepared on Ag-metalized substrate.

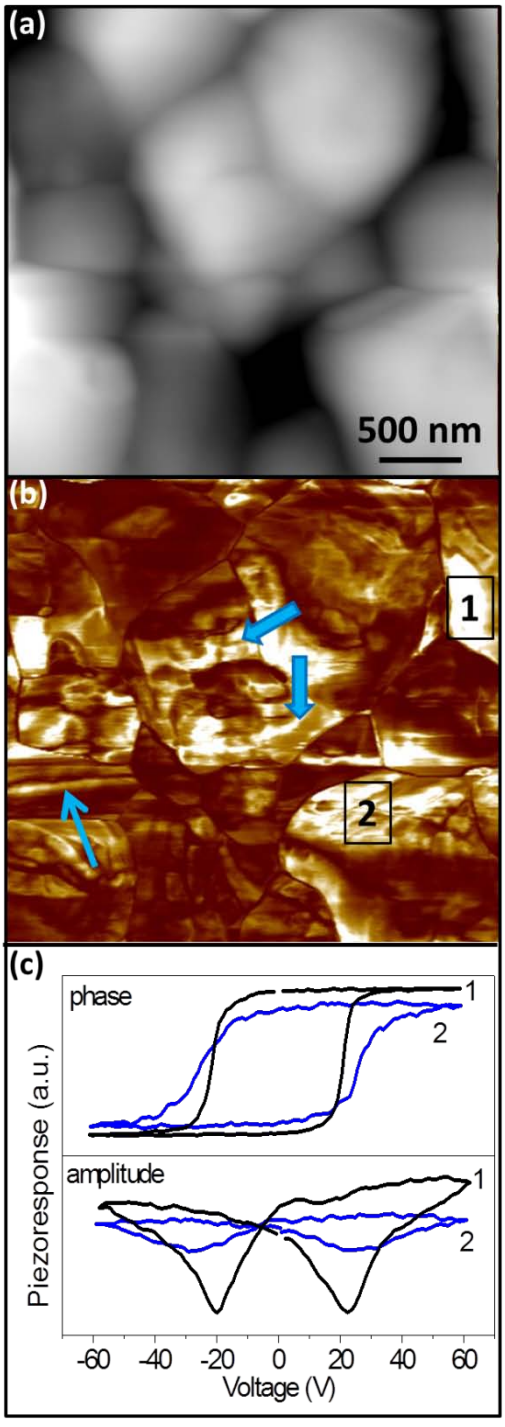

Fig. 3: (a) Topography and (b) out-of-plane PFM amplitude image of the PMN–35PT thick film on substrate. (c) PFM amplitude and phase hysteresis loops obtained from the areas marked by no. 1, 2 in the panel (b)

The films exhibited high piezoelectric properties, with the piezoelectric coefficient d33 up to 120 pC/N, reasonable for piezoelectric energy harvesting applications.

Further study will be allocated towards obtaining effective active elements for micro-electro-mechanical systems for piezoelectric energy harvesting.

V. ACKNOWLEDGMENT

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