

Thin pyroelectric PLZT film obtained with sol-gel technology

Andrzej Łoziński

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Abstract The sol-gel technology (J. Zarzycki in J.Sol-Gel Sci. Technol. 8:17–22, 1997) and the spin coating were employed for the production of PLZT 12/40/60 pyroelectric film. The starting materials were: lead acetate, lanthanum nitrate, metallo-organic compounds of zirconium and titanium and acetic acid. An alumina substrate with pre-deposited lanthanum-strontium cobalt oxide (LSCO) (H. Takahashi, et al in Phys. Rev. B. 57:15211–15218, 1998) bottom electrode was spin-coated with a sol several times. Following, the film was rapidly thermally processed. To obtain a continuous PLZT film these two operations were repeated a few times. The top electrode, made from LSCO, was subsequently applied on the PLZT film. The produced film has a lower pyroelectric coefficient than bulk ceramics and thick films formerly produced. Figure of merit F_v , relating to the voltage responsivity is higher than those of the two earlier materials, due to much lower relative permittivity. The important advantage of applied method is that it requires much lower processing temperature (680°C) than that (1,150°C) needed to produce bulk and thick-film sensors.

Keywords Pyroelectrics · Ferroelectrics · PLZT ceramics · Sol-gel

1 Introduction

Our earlier promising results of the utilisation of perovskite-type lead lanthanum zirconate titanate (PLZT)

ceramics as both bulk [3] and thick-film [4] material for pyroelectric sensors promoted this work to devise a method for the production of thin-film pyroelectric sensors from this ceramics. In this case the term thin-film concerns rather the method of production than the thickness of finally obtained film.

In the synthesis, the following commercially available chemicals were employed: lead acetate $[\text{Pb}(\text{CH}_3\text{COO})_2 \times 3 \text{H}_2\text{O}]$, lanthanum nitrate $\text{La}(\text{NO}_3)_3 \times 6 \text{H}_2\text{O}$, zirconium propoxide $[\text{Zr}(\text{C}_3\text{H}_7\text{O})_4]$, titanium isopropoxide $[\text{Ti}(\text{OC}_2\text{H}_4\text{CH}_3)_4]$, 2-methoxyethanol $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and acetic acid CH_3COOH . The last chemical was a solvent.

The sol-gel technology and the spin coating employed here allowed thin ceramic layers to be obtained. This method is particularly advantageous in the preparation of lead containing films because the temperatures needed for sintering are lower than lead evaporation temperature.

2 Experiment

The tetragonal PLZT 12/40/60 composition was used here. This notation means that there is a substitution of 12 at. % of the lanthanum La^{3+} ions for the lead Pb^{2+} ions, and the zirconium to titanium Zr/Ti ratio is 40/60. This composition has moderate permittivity, relatively low electrical loss and large pyroelectric coefficient [3, 4].

The composition was calculated according to the formula $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ [5].

As substrate an alumina (99,8% Al_2O_3) plate pre-deposited with lanthanum-strontium cobalt oxide (LSCO) thin-film bottom electrode was used. The electrode production based on the so-gel technology from water solution of lanthanum, strontium and cobalt nitrates with addition of

A. Łoziński (✉)
Department of Optoelectronics,
Gdańsk University of Technology,
Narutowicza 11, PL 80-952 Gdańsk, Poland
e-mail: alozi@pg.gda.pl

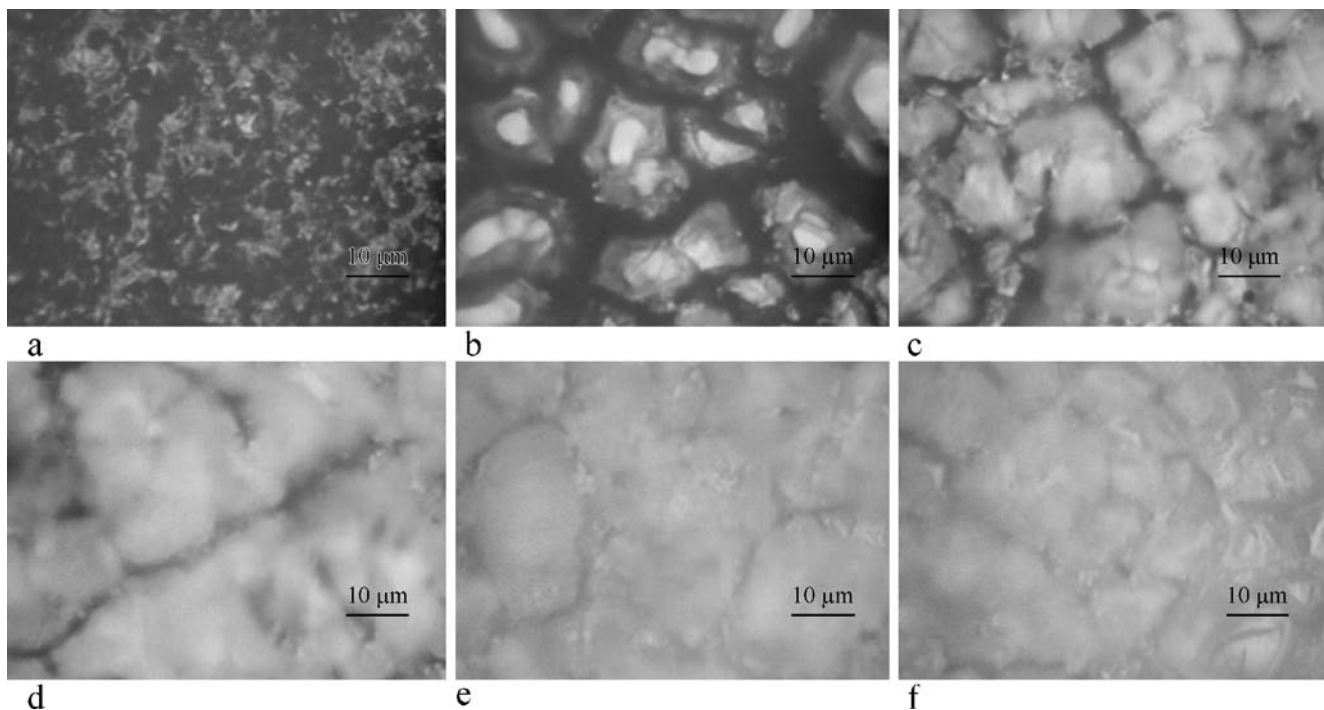


Fig. 1 The micrographs of: **a** LSCO electrode, **b** ÷ **f** 1, 2, 3, 6, and 10 PLZT films, respectively

polyvinyl alcohol and glycine [6]. The substrate was spin-coated with this solution and subsequently thermally processed at 650°C for 90 s.

Each PLZT film was set by spin-coating at 1,500 rpm for 60 s followed by an additional 120 s spin to dry the films. Each ten films were then rapidly thermally processed (RTP) at 650°C for 90 s. Ramping from room temperature to 650°C lasted about 90 s. After the RTP the PLZT film was shrinking, forming the separate crystallites on the LSCO electrode. To obtain a continuous PLZT film, these operations were repeated ten times and then the films were annealed at 680°C for 5 min. Figure 1 a – f shows the micrographs of LSCO film and 1, 2, 3, 6 and 10 PLZT films, respectively. The thickness of the final film was about 30 μm.

Figure 2 shows the flow chart for complete PLZT film preparation, including the sol-gel process. The top electrode was also made from LSCO. High emissivity of LSCO top electrode (0.98) causes good absorption of falling radiation. The obtained structure was polarised with 2 V/μm field for half an hour in room temperature.

3 Measurements

Relative permittivity was determined from the capacitance measurements, using an automatic C-bridge at 1 kHz frequency at 0.5 V voltage. The investigated sample was placed in a thermal chamber with a temperature readout

facility. The same equipment allowed to determine the dielectric loss under the same conditions.

The pyroelectric coefficient p was determined as a temperature-dependent change of material spontaneous polarisation P , i.e. $p = dP/dT$, where dP/dT is the temperature derivative of spontaneous polarisation. A computer-

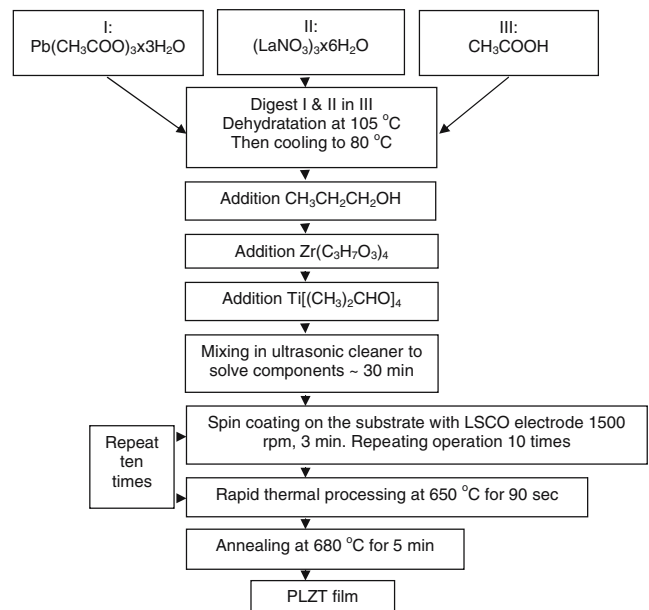


Fig. 2 Flow chart for PLZT film preparation

Table 1 The comparison of parameters of PLZT 12/40/60 composition produced in various technologies.

Material PLZT 12/40/60	ϵ at room temp.	$\tan\delta$ at room temp.	p C/m ² K ($\times 10^{-4}$)	c' J/m ³ K ($\times 10^6$)	F_V Cm/J ($\times 10^{-13}$)	F_D Cm/J ($\times 10^{-11}$)
Bulk	1,129	0.015	3,5	3.4	0.91	2.5
Thick-film	190	0.014	1.5	1.7	4.64	5.41
Thin-film	30	0.02	0.3	2.1	4.76	1.84

aided method allowed determination of the coefficient p as a function of temperature. This method permits automatic measurement and data handling and is based on the continuous measurement of the voltage drop caused by the pyroelectric current when the examined element is subjected to a slowly ramping temperature. The voltage drop is developed across a $10^8 \Omega$ calibrated shunting resistor. This value is at least four orders lower than the dc resistance of the treated sample.

4 Results and discussion

The applied technology resulted in 30 μm thick pyroelectric film with the following parameters: room temperature relative permittivity $\epsilon = 30$, loss tangent = 0.02, pyroelectric coefficient $p = 3 \times 10^{-5} \text{C/m}^2\text{K}$. The pyroelectric coefficient of thin-film is smaller than those of bulk ceramics and thick-films of the same composition, but as a result of the much lower permittivity, the figures of merit $F_V = p/(\epsilon c')$ and $F_D = p/(\epsilon \tan\delta)$, (c' -volume specific heat, ϵ -relative permittivity, $\tan\delta$ -loss), are similar. F_V describing the voltage responsivity is high, while F_D describing the detectivity of the pyroelectric material is little lower. Both figures of merit are defined slightly unlike the usual practice [7]. The permittivity of free space is omitted, as

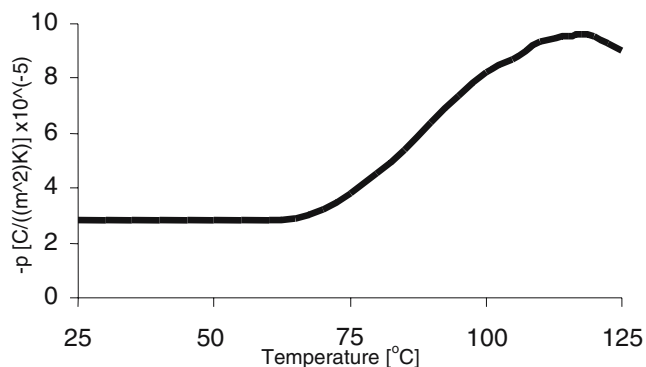


Fig. 3 Temperature dependence of pyroelectric coefficient of the PLZT 12/40/60 film polarised with 2 V/ μm

we cannot control this value. The comparison of these parameters with those of the previously made bulk and thick-film materials of the same composition is shown in Table 1 [3, 4].

Figure 3 shows the temperature dependence of the pyroelectric coefficient of the described film.

No any delaminating effect on the bottom electrode was observed after the crystallisation of the three μm thick film. Also using gold as a bottom electrode instead of LSCO did not cause any delaminating effect. The lack of delaminating effect could be probably explained due to release stress when first rapidly thermally treated layer forms separate “islands” instead of continuous film (Fig. 1b). Figure 4 shows the X-ray diffraction pattern of the bulk ceramics produced earlier, while Fig. 5 presents the pattern of the film obtained with the described method, deposited on the alumina substrate with the gold electrode.

Both figures indicate the PLZT perovskite phase is well crystallised. In both cases crystallites are randomly oriented. Much lower permittivity of the thin film can be explained by its lower density. The bulk ceramics was vacuum hot pressed [8] and nearly theoretical density was obtained.

5 Conclusions

Due to the elaborated technology the pyroelectric sensor can be obtained. The processing temperature (maximum

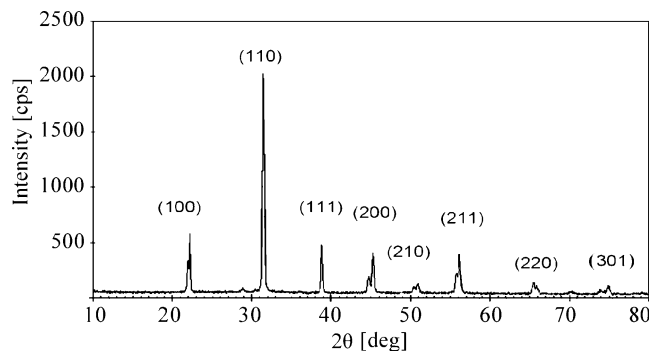


Fig. 4 XRD profile of bulk PLZT 12/40/60

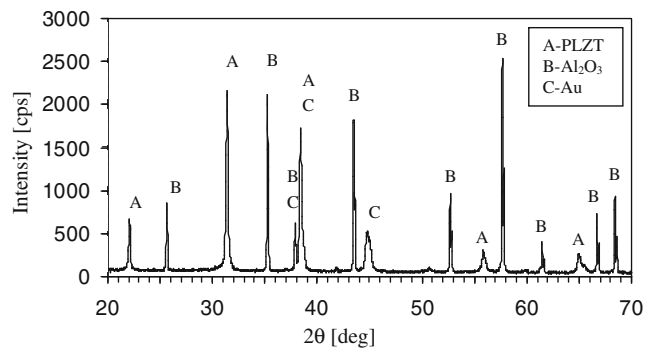


Fig. 5 XRD profile of PLZT 12/40/60 film deposited on an alumina substrate with a gold bottom electrode

680°C), is much lower than that needed to produce bulk and thick-film sensors, (1,150°C), as reported previously [3, 4]. This is an important advantage as a maximal temperature of sintering is lower than the lead evaporation temperature. Figure of merit F_V relating to the voltage responsivity is higher than this of the thick-film material. Figure of merit F_D relating to the noise parameters is

slightly worse. Advantageous high emissivity of LSCO electrode causes high absorption of falling radiation.

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References

1. J. Zarzycki, *J. Sol-Gel Sci. Technol.* **8**, 17–22 (1997)
2. H. Takahashi, et al., *Phys. Rev., B* **57**, 15211–15218 (1998)
3. A. Łoziński, H. Wierzba, in *Optoelectronic and Electronic Sensors: Proceedings SPIE*, **2634**, 59–62 (1994)
4. A. Łoziński, et al., *Meas. Sci. Technol.* **8**, 33 (1997)
5. C. Land, P. Thacher, G. Hartling, *Appl. Solid State Science*, **4** (Academic, New York, 1974), p. 178
6. F. Wang, A. Uusimäki, S. Leppävuori, *Appl. Phys. Lett.* **67**, 1692 (1995)
7. R. Whatmore, *Rep. Prog. Phys.* **49**, 1335–1386 (1986)
8. A. Łoziński, in *Photovoltaic and Optoelectronic Processes: Proceedings CIP*, **5**, 69–72 (1984)