Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 30 (2010) 1437–1444
www.elsevier.com/locate/jeurceramsoc

0.65Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.35$PbTiO_3$ thick films prepared by electrophoretic deposition from an ethanol-based suspension

Danjela Kuscer*, Marija Kosec

Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Received 23 June 2009; received in revised form 16 October 2009; accepted 2 November 2009
Available online 2 December 2009

Abstract

We have investigated the processing of 0.65Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.35$PbTiO_3$ (denoted PMN–PT) thick films using an electrophoretic deposition process (denoted EPD), with the PMN–PT particles suspended in an ethanol-based suspension. The zeta-potential and the viscosity were measured to identify the conditions for the preparation of a stable suspension suitable for the EPD. The applied voltage, the deposition time, the chemical composition of the suspension and the concentration of the powder were investigated in order to obtain a high-quality PMN–PT deposit with a target thickness of about 50 μm. The PMN–PT thick films prepared from stoichiometric and PbO-excess suspensions by sintering at 950 and 1100 °C were examined by X-ray powder-diffraction analysis and scanning electron microscopy. The highest functional response was obtained for a homogeneous, dense, crack-free PMN–PT thick film prepared from a PMN–PT suspension with excess PbO. The film was deposited at a constant voltage of 10 V and for a time of 120 s, followed by sintering at 1100 °C in a PbO-rich atmosphere. The film's properties were as follows: a dielectric permittivity ε of 20,250 at a T_m of 172 °C, a remanent polarization of 17 μC/cm^2 and a coercive field of 5 kV/cm.

Keywords: Films; Suspensions; Microstructure-final; Ferroelectric properties; Perovskites; Niobates

1. Introduction

Lead-based perovskite ceramics have generated significant interest because of their outstanding piezoelectric properties, which are utilized in various electronic devices, such as multilayer capacitors, sensors, actuators and electro-optical devices. Among them 0.65Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.35$PbTiO_3$ (PMN–PT) has been widely investigated because of its high dielectric constant. For the latest applications, the final device should be reliable, reasonably priced as well being as small as possible. As a result, the components are designed in the form of thin layers integrated into the substrate. Electrophoretic deposition has been shown to be a successful method for the preparation of homogeneous and reliable ceramic films on a substrate with thicknesses ranging from a few micrometres to a few millimetres by using simple and low-cost equipment.[1]

A stable colloid with well-dispersed particles, an optimised deposition process and the best sintering conditions are necessary if we wish to obtain a final product with the desired properties. It is known, for example, that the electrosteric stabilisation of ceramic particles is easier in water, but that water-based suspensions are prone to the hydrolysis of water at potentials above 2 V.[2] For the processing of PMN–PT thick films by electrophoretic deposition, therefore, non-aqueous suspensions are preferable over water-based suspensions since the hydrolysis of water at the electrodes can be avoided in this way. Moreover, it was shown that in water, both lead and magnesium ions preferentially dissolve from the PMN's surface in the pH range between 2 and 10.[3] Therefore, the leaching of Pb^{2+} and Mg^{2+} in water is a major issue in the colloidal processing of PMN–PT using an aqueous medium.

The electrophoretic deposition of 0.8Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.2$PbTiO_3$ particles onto platinum foils has been reported by Chen et al.[4,5] The micron-sized powder was dispersed in ethanol using only an ultrasound treatment, and for the deposition they used a constant voltage of 100 V for 2 min. A dense, 16-μm thick film with a dielectric permittivity of 26,000 at a T_m of 100 °C was obtained after sintering at 1100 °C.[4]

In the colloidal processing of ceramic powders, ammonium polyacrylate is a widely used dispersant in aqueous media.[6–8]

* Corresponding author. Tel.: +386 1477 3489; fax: +386 1477 3887.
E-mail address: danjela.kuscer@ijs.si (D. Kuscer).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.11.002

The adsorption mechanism of polyacrylic acid on PMN particles in an aqueous medium was proposed by Sakar-Deliormanli.[9] For the adsorption process above the isoelectric point, pH_{IEP}, chemical interactions between the ionized carboxyl group and the $M^{2+}OH$ as well as the hydrogen bonds are responsible. Below the pH_{IEP} the carboxylic group is bonded to the positively charged PMN particles due to the hydrogen bonds and the electrostatic interactions. However, ammonium polyacrylate is not soluble in ethanol and therefore some modifications are reported. Popa et al.[10,11] studied the colloidal stability of Al_2O_3 and ZrO_2 particles in ethanol. They used an ammonium salt of poly-methacrylic acid that enables particle charging and the electrosteric stabilization of the suspension. An organic base n-butylamine was used to dissociate the ammonium salt of the poly-methacrylic acid.

In order to achieve a high-quality thick-film structure with a homogeneous microstructure, it is necessary to control not only the properties of the suspensions but also the sintering conditions.[12] This study was oriented toward guaranteeing good adhesion between the substrate and the PMN–PT layer as well as preventing the chemical reactivity between the components. In addition, the PMN–PT layer has to be dense in order for it to display a satisfactory functional response.[13] It was shown that the densification of lead-based perovskite thick films can be improved considerably by the presence of a PbO liquid phase. This liquid phase can then be removed from the film by careful control of the atmosphere during the sintering.[13–15]

The aim of our work was to study the processing of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ (PMN–PT) thick films on platinized alumina substrates using the electrophoretic deposition process. The colloidal stability of PMN–PT particles in ethanol, the deposition process and the sintering conditions were taking into account in order to produce high-quality thick-film structures with a suitable functional response.

2. Experimental

The $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ powder was prepared using a high-energy milling process. A mixture of PbO (99.9+%, Aldrich, Steinheim, Germany), MgO (98%, Aldrich, Steinheim, Germany), TiO_2 (99.8%, Alfa Aesar, Karlsruhe, Germany) and Nb_2O_5 (99.9%, Aldrich, Steinheim, Germany) in the molar ratio corresponding to the stoichiometry of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ was high-energy milled in a planetary mill (Retsch, Model PM 400, Hann, Germany) for 64 h. Experimental details together with the properties of the powder are given in.[16,17]

The suspension was prepared by dispersing the PMN–PT powder, prefired at 700 °C for 2 h in a solution of anhydrous ethanol (Carlo Erba, Milano, Italy), Darvan 821 A (R.T. Vanderbilt Co., Norwalk, USA) containing 40 wt% of ammonium polyacrylate with a molecular weight of 3500 and 60 wt% of water (denoted ammonium polyacrylate) and an organic base n-butylamine (Alfa Aesar, Karlsruhe, Germany). The following procedure was used. The calculated amount of ammonium polyacrylate was mixed with calculated amount of n-butylamine and added to the ethanol. The PMN–PT powder mixed with ethanol was than added to the solution. Powder concentrations of 5 and 20 vol.% were used for the preparation of the suspension. The amounts of ammonium polyacrylate and n-butylamine are expressed in millilitres per gram of PMN–PT powder (denoted ml/g s.l.).

All the suspensions were homogenized in a ZrO_2 planetary mill (Retsch, Model PM 400, Hann, Germany) for 1 h at 100 rpm.

In order to determine the optimum amount of ammonium polyacrylate and n-butylamine, two types of suspensions with a PMN–PT concentration of 5 vol.% were prepared. The first set of experiments was performed with a constant amount of ammonium polyacrylate (0.01 ml/g) and various amounts of n-butylamine, i.e., 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0 ml/g. The second set of experiments was performed with a constant amount of n-butylamine (0.01 ml/g) and various amounts of ammonium polyacrylate, i.e., 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0 ml/g.

The deposition was performed from two kinds of PMN–PT suspensions. First, the PMN–PT powder was suspended in ethanol using 0.01 ml of ammonium polyacrylate/g and 0.01 ml of n-butylamine/g. This suspension is referred to as PMN–PT. Second, a PMN–PT suspension with 2 mol% of PbO (referred to as PMN–PT 2% PbO) was prepared by mixing a PMN–PT suspension with a PbO suspension in the corresponding stoichiometry. The PbO suspension was prepared from PbO powder, ethanol, 0.01 ml of ammonium polyacrylate/g PbO and 0.01 ml of n-butylamine/g PbO. It contained 5 vol.% of PbO.

The zeta-potentials of the suspensions were measured at room temperature using a zeta-potential analyser (ZetaPals, Brookhaven Instruments). The viscosity measurements were performed at 20 °C using a viscosimeter (Haake, viskotester VT 500) with an MV 1 sensor system.

The electrophoretic deposition (denoted EPD) was performed at room temperature in an electrode cell with a platinum cathode and a platinized PZT/Al_2O_3 substrate that acts as the anode. The surface area of the anode was 1.7 cm^2, and the distance between the electrodes was fixed at 25 mm. The EPD was carried out by applying a DC electric field between the electrodes using the constant-voltage mode. The process was carried out at a fixed voltage of 10, 20, 30, 40, 50 or 60 V and a deposition time of up to 120 s. The deposits were dried in a Petri dish at room temperature in an ethanol-rich atmosphere.

The PMN–PT mass deposited on the substrate under certain deposition conditions was quantified by measuring the weight of the deposit gained after the deposition. The weight of the substrate before the deposition and the weight after the deposition and drying were measured using a digital balance (Mettler Toledo) with a 0.0001 g resolution.

In order to study the sintering procedure, the PMN–PT and the PMN–PT 2% PbO were deposited on a platinized PZT/Al_2O_3 substrate using a 10-V constant-voltage mode and a deposition time of 120 s. After the drying, the thick-film structures were sintered at 950 and 1100 °C for 2 h in a PbO-rich atmosphere. The samples were placed in a covered corundum vessel and packing powder with the composition $PbZrO_3$ plus 2 mol% excess of PbO were placed around the thick-film structure.

The X-ray powder-diffraction data were collected at room temperature on a diffractometer (PANalytical, X'Pert PRO

MPD, The Netherlands) using Cu Kα radiation. The data were collected in the 2θ range from 10° to 70°, in steps of 0.034°, with an integration time of 100 s. The phases were identified using the PDF-2 database.[18] The lattice parameters of the PMN–PT were calculated on the basis of a tetragonal unit cell, as proposed by Kumar and Pandey[19] using the Topas R (Bruker AXS, Karlsruhe, Germany) software package.

The microstructures of the sintered deposits were characterized with a scanning electron microscope (JEOL 5800, Tokyo, Japan), equipped with a Tracor-Northern energy-dispersive system (EDS).

The density was calculated by a quantitative characterisation of the ceramic microstructure using the computerised image-analysis software ImageTools 3.0 (The University of Texas Health Science Center in San Antonio, USA). The binary image obtained from the original micrograph was used to determine the quantity of pores.

Gold electrodes were sputtered onto the thick films for the electrical measurements. The real and the imaginary parts of the complex dielectric constant were measured with a HP 4284 A Precision LCR Meter in the frequency range from 1 up to 1000 kHz for temperatures from 20 to 300 °C. The heating rate was 1–2 °C/min.

The values of the remanent polarisation and the coercive field were determined from ferroelectric hysteresis curves measured with an Aixact TF Analyser 2000.

3. Results and discussion

3.1. Characterization of suspension

The zeta-potential of the PMN–PT in ethanol at a constant concentration of 0.01 ml n-butylamine/g as a function of the ammonium polyacrylate is shown in Fig. 1a. A positive zeta-potential was measured for the PMN–PT particles in ethanol at a low concentration of ammonium polyacrylate. However, with increasing amounts of ammonium polyacrylate the zeta-potential becomes negative and its absolute value increases up to 0.01 ml ammonium polyacrylate/g. With further additions it remains constant at a value of approximately −30 mV.

Similar zeta-potential behaviour is observed for the PMN–PT particles dispersed in ethanol at a constant amount of 0.01 ml ammonium polyacrylate/g as a function of the amount of n-butylamine (Fig. 1b). The zeta-potential of PMN–PT is slightly positive for small amounts of n-butylamine, but this becomes negative when the amount increases. The absolute value of the zeta-potential of the PMN–PT particles in ethanol increases almost linearly with the increasing amount of n-butylamine from 0 to 0.01 ml/g; however, between 0.01 and 0.02 ml/g it is almost constant with a value of approximately −30 mV.

From these measurements it is evident that the zeta-potential of the PMN–PT particles is positive for small amounts of n-butylamine and 0.01 ml/g ammonium polyacrylate and for small amounts of ammonium polyacrylate and 0.01 ml/g n-butylamine. The positive zeta-potential of the PMN–PT particles can be explained by the acidic character of the ethanol. The small amount of water that is introduced into the system with the addition of the ammonium polyacrylate solution in water seems to be sufficient to generate free protons, which are then adsorbed onto the PMN–PT particles. As a result, the particles are positively charged. The slightly positive zeta-potential of the particles in the ethanol has also been reported for other systems, such as yttria-stabilized ZrO_2.[20]

When larger amounts of ammonium polyacrylate and n-butylamine were added to the suspension the zeta-potential of the PMN–PT became negative and the absolute value increased. This indicates that the surfaces of the particles are negatively charged. Popa et al.[11] studied alumina- and zirconia-based suspensions in ethanol and they reported that when adding n-butylamine to the ethanol-based suspension the ammonium polyacrylate dissociates and gets adsorbed onto the alumina particles. It is known that the ammonium polyelectrolytes in alkaline suspensions dissociate and absorb onto the Al_2O_3 particle surfaces, which consequently increases the stability of the Al_2O_3 suspension in ethanol.[6] By adding n-butylamine to the ethanol-based suspension, the base character of the suspension is introduced, since n-butylamine is an organic base with a pK_a of 12.5 at 20 °C. We have observed that ammonium polyacrylate is not soluble in pure ethanol; however, a mixture of ammonium polyacrylate and n-butylamine is. We assumed that ammonium polyacrylate in the presence of n-butylamine dissociates and gets adsorbed onto the PMN–PT particles. As a result, the PMN–PT particles become negatively charged.

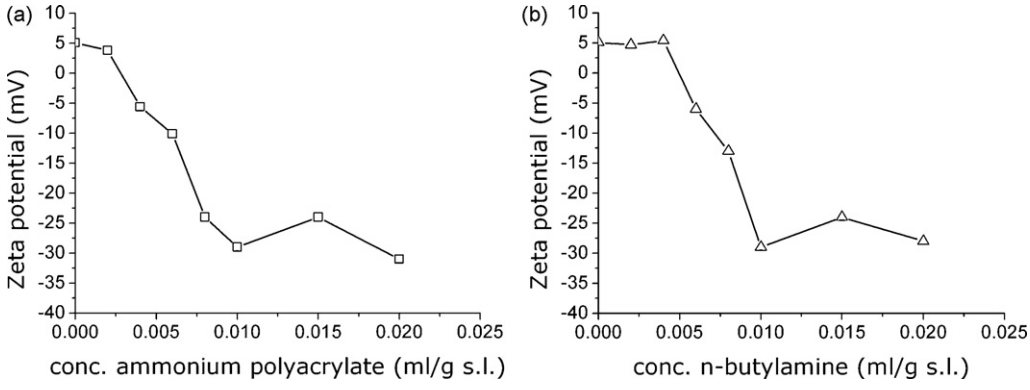

Fig. 1. Zeta-potential of PMN–PT in ethanol at (a) 0.01 ml/g s.l. n-butylamine as a function of ammonium polyacrylate and (b) 0.01 ml/g s.l. ammonium polyacrylate as a function of n-butylamine. The amount of n-butylamine and ammonium polyacrylate is given as the volume (ml) per gram of PMN–PT powder (g s.l.).

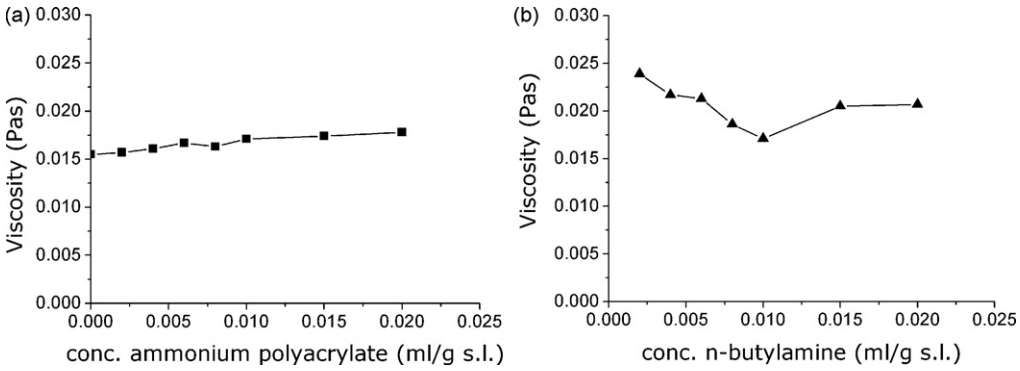

Fig. 2. Viscosity of PMN–PT in ethanol at (a) 0.01 ml/g s.l. n-butylamine as a function of ammonium polyacrylate and (b) 0.01 ml/g s.l. ammonium polyacrylate as a function of n-butylamine. The amount of n-butylamine and ammonium polyacrylate is given as the volume (ml) per g of PMN–PT powder (g s.l.).

The viscosity of the PMN–PT suspension at a constant amount of 0.01 ml n-butylamine/g as a function of the amount of ammonium polyacrylate is shown in Fig. 2a. The viscosity of the suspension increases slightly with the increasing amount of ammonium polyacrylate, from 15.5 to 17.8 mPa s at 0 and 0.02 ml ammonium polyacrylate/g, respectively.

The viscosity of the PMN–PT suspension at a constant amount of 0.01 ml ammonium polyacrylate/g as a function of the amount of n-butylamine is shown in Fig. 2b. The viscosity of these suspensions is higher than the viscosity of the suspensions with a constant amount of n-butylamine. With the increasing amount of n-butylamine the viscosity decreases, showing a minimum value at 0.01 ml n-butylamine/g. With further additions the viscosity increases. The addition of 0.002, 0.1 and 0.2 ml n-butylamine/g results in viscosities of 24, 17 and 21 mPa s, respectively.

We assume that at a low concentration of n-butylamine, only a part of the ammonium polyacrylate is dissociated. A free polymer ammonium polyacrylate can form bridges with the adsorbed polymer on the particles, as reported by Popa et al.,[11] and as a result the viscosity is high. When a larger amount of n-butylamine is present in the suspension, the ammonium polyacrylate further dissociates and, simultaneously, the amount of free polymer decreases. As a result the viscosity also decreases. At the optimum concentration of n-butylamine, the viscosity reaches the minimum value.

With a larger amount of n-butylamine the viscosity of the PMN–PT suspensions increases possibly due to the higher ionic strength of the suspension. A similar phenomenon was observed by Popa et al.[10] in an Al_2O_3 powder suspended in ethanol. They assumed that for a larger amount of n-butylamine the viscosity increases due to the higher ionic strength of the suspension, resulting in a compression of the double layer.

From the zeta-potential and viscosity measurements we can conclude that the effective medium for PMN–PT particles suspended in ethanol is the addition of both ammonium polyacrylate and n-butylamine/g with a concentration of 0.01 ml/g PMN–PT.

We have measured the zeta-potential of PbO particles in a PbO suspension. Its value of −40 mV is slightly higher than that of the PMN–PT particles, i.e., −30 mV. We assume that both PbO and PMN–PT particles move under an applied voltage to the anode, where both of them are deposited.

3.2. Electrophoretic deposition

Further experiments were performed from freshly prepared PMN–PT suspensions containing 5 and 20 vol.% of the solid load (denoted PMN–PT and PMN–PT 20, respectively) and from the PMN–PT 2% PbO suspension with a 5 vol.% solid load (denoted PMN–PT 2% PbO). The optimum concentration of 0.01 ml/g of both ammonium polyacrylate and n-butylamine was used.

Fig. 3 shows the mass of the deposit as functions of the applied voltage and the powder concentration attained after 10 and 30 s of the deposition. The weight gains increase monotonically with the increasing applied voltage. The higher applied voltage, the longer deposition time and/or the higher concentration of the powder in the suspension give rise to higher deposition yields. These observations are in accordance with the mechanism of the electrophoretic deposition, which stated that the mass gained during the deposition depends on the dielectric constant and the viscosity of the solvent, the solid load, the zeta-potential of the particles in suspension, the geometry of the system and the applied voltage.[1,21]

From the results it is evident that the mass gained from 5 vol.% suspension and an applied voltage between 10 and 60 V is, after 30 s of deposition, always about three times higher than that after 10 s of the deposition. This is in accordance with the

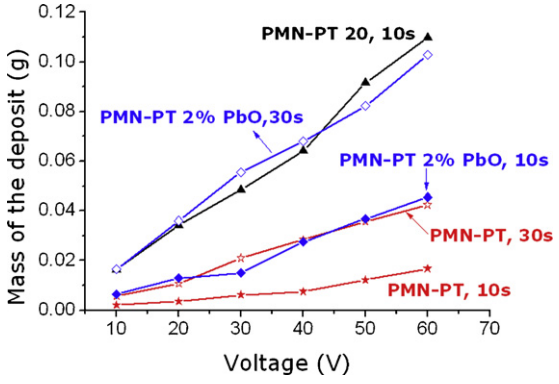

Fig. 3. PMN–PT deposition mass versus voltage from 5 vol.% suspensions of PMN–PT and PMN–PT 2% PbO for deposition times of 10 and 30 s and from a 20 vol.% suspension PMN–PT (denoted PMN–PT 20) for a deposition time of 10 s.

Hamaker's equation, which states that the mass of the deposit increases linearly with the increasing deposition time if the other parameters are constant.[21] However, when increasing the particle concentration from 5 to 20 vol.% the mass of the deposit does not increase proportionally. All the deposits prepared from the 5 vol.% suspension with a deposition time of 10 s were continuous and uniform without any cracks.

From Fig. 3 it is evident that the deposition yield from lead-containing suspensions, e.g., PMN–PT 2% PbO, is higher than that from PMN–PT. The explanation for this phenomenon may be the higher electrophoretic mobility of PbO than that of PMN–PT, since the zeta-potential of PbO is slightly higher than that of PMN–PT. We believe that in PMN–PT 2% PbO suspensions the overall mobility is higher than in PMN–PT suspensions, which is reflected in the higher deposition yield from PbO-containing PMN–PT suspensions. Similar observations are reported by Put et al.,[22] who studied the electrophoretic deposition of alumina and zirconia mixtures. They reported that the electrophoretic mobility of Ce–ZrO_2 powder is higher than that of Al_2O_3 powder and that the electrophoretic mobility of particles in an Al_2O_3/Ce–ZrO_2 mixture is comparable to that of Ce–ZrO_2. From these results it is evident that in an Al_2O_3/Ce–ZrO_2 mixture the powder with the highest electrophoretic mobility determines the overall mobility.

We observed that for higher particle concentrations, longer deposition times and/or higher applied voltages the deposit tends to crack. This was the case for thicker films prepared from the PMN–PT 20 suspension containing 20 vol.% of particles using a deposition time longer than 10 s and high applied voltages. We believe that the thicker coatings are more prone to cracking under the drying conditions we used. Uniform, homogeneous, crack-free deposits with the desired thickness have been processed under our experimental conditions by using a low powder concentration, low applied voltages and long deposition times.

3.3. Sintering of the thick-film PMN–PT structures

The thick-film structures prepared from the PMN–PT and PMN–PT 2% PbO suspensions were sintered at 950 and 1100 °C for 2 h in a lead-rich atmosphere. The particles were deposited on a PZT/Pt/Al_2O_3 substrate using an applied voltage of 10 V for 120 s.

The sintered PMN–PT thick films were then investigated by X-ray powder-diffraction (XRD) analyses. The XRD patterns of the PMN–PT and PMN–PT 2% PbO sintered at 950 and 1100 °C are shown in Fig. 4. All the diffraction peaks match the perovskite structure. We did not observe any additional peaks that might correspond to the pyrochlore phase, which commonly accompanies the formation of lead-based perovskites, or to the PbO phase.

The lattice parameters of the PMN–PT thick films are shown in Table 1. They were indexed based on a tetragonal symmetry with the space group *P4mm*.[19] It is evident that the lattice parameters of all the samples are similar, within the experimental uncertainty. They agree well with the reported values for the bulk as well as for screen-printed thick films that have the composition $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$.[12,19] These results indicate

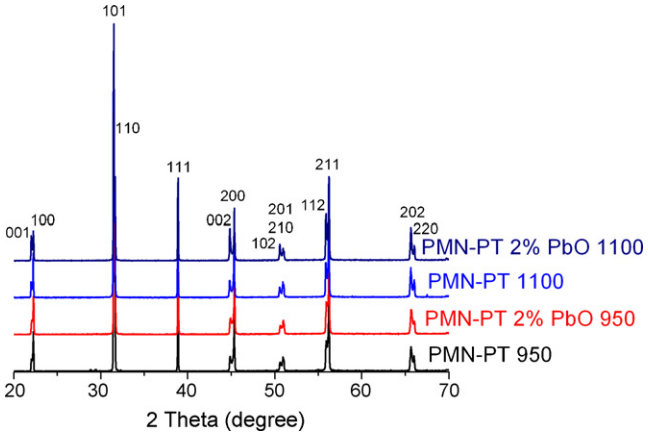

Fig. 4. X-ray powder-diffraction pattern of PMN–PT and PMN–PT 2% PbO sintered at 950 and 1100 °C.

that the chemical composition of all the investigated PMN–PT thick films is similar and does not change during the deposition or sintering processes.

The polished cross-sections of the PMN–PT and the PMN–PT 2% PbO on the PZT/Pt/Al_2O_3 substrates sintered at 950 and 1100 °C are shown in Figs. 5 and 6, respectively. In our previous study we found that the PZT layer deposited between the Al_2O_3 substrate and the platinum electrode serves as a barrier layer that prevents the diffusion of aluminium ions into the active PMN–PT layer as well as the diffusion of lead ions from the PMN–PT into the alumina.[12] It was also observed that the adhesion of the screen-printed PMN–PT to the Pt/PZT/Al_2O_3 substrate is improved. The lead-aluminate-based crystals (denoted $PbAl_{11}O_{19}$) that were detected at the Al_2O_3/PZT interface did not cause the delamination of the PZT/Pt/PMN–PT layer from the alumina substrate. The results of this investigation confirmed that the PMN–PT layer deposited by electrophoresis onto the Pt/PZT/Al_2O_3 substrate exhibits good adhesion with the platinum electrode and that the chemical composition of the PMN–PT was not changed during the processing. From the electron microscopy backscattered images (SEM/BEI) it is evident that the PMN–PT thick film contains some pores that are homogeneously distributed in the PMN–PT matrix. We did not, however, detect any extra phases in the PMN–PT layer with this method.

Since the PMN–PT layer is clamped to the substrate, it can shrink in the direction perpendicular to the substrate during the

Table 1
Lattice parameters of PMN–PT and PMN–PT 2% PbO sintered at 950 and 1100 °C.

	950 °C	1100 °C
PMN–PT		
a (nm)	0.40045 ± 0.00003	0.40047 ± 0.00004
c (nm)	0.40391 ± 0.00004	0.40385 ± 0.00004
a/*c*	0.991	0.991
PMN–PT 2% PbO		
a (nm)	0.40049 ± 0.00003	0.40051 ± 0.00006
c (nm)	0.40386 ± 0.00004	0.4039 ± 0.0001
a/*c*	0.991	0.991

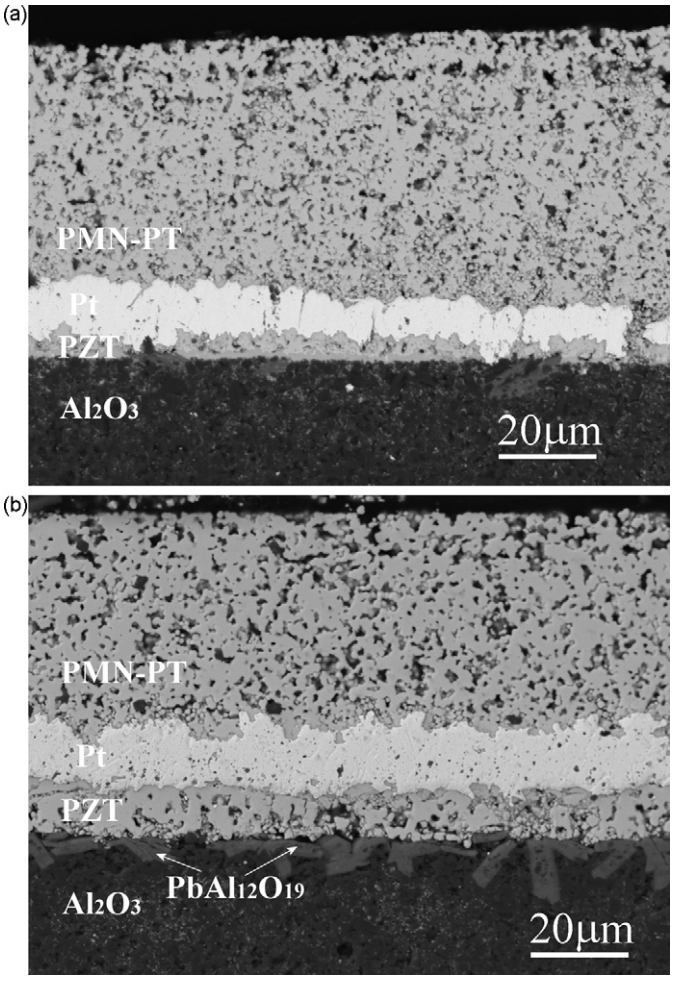

Fig. 5. SEM/BEI image of polished cross-section of PMN–PT/PZT/Pt/Al_2O_3 thick-film structure sintered in lead-rich atmosphere at (a) 950 °C and (b) 1100 °C.

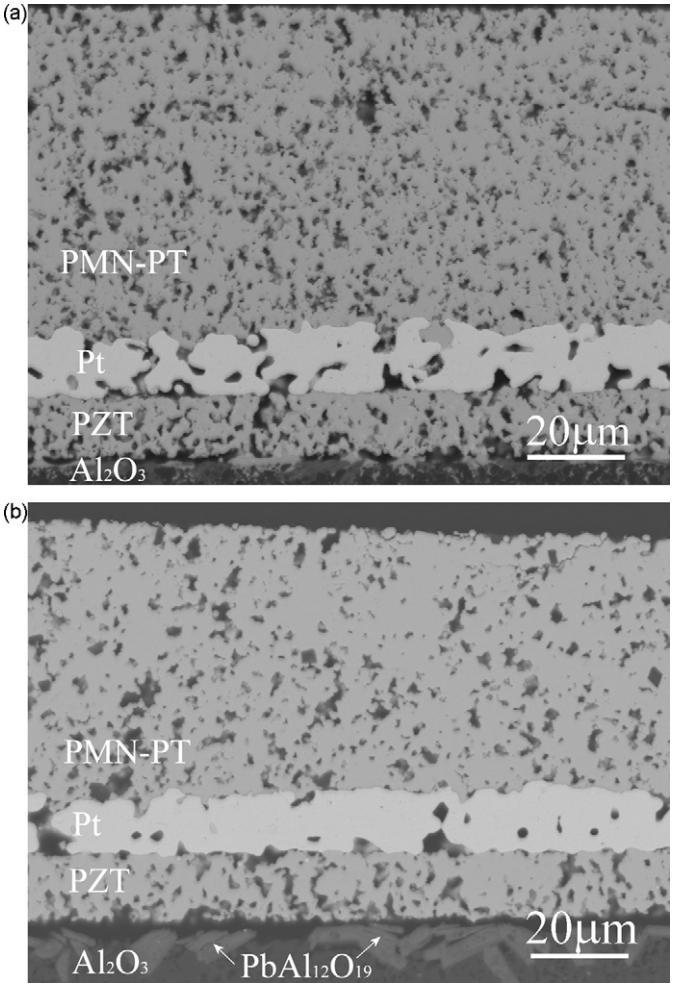

Fig. 6. SEM/BEI image of polished cross-section of PMN–PT 2% PbO/PZT/Pt/Al_2O_3 thick-film structure sintered in a lead-rich atmosphere at (a) 950 °C and (b) 1100 °C.

sintering process. Therefore, the thinner the layer, the denser the thick-film structure should be. The thickness of the layers together with the density obtained from the microstructural analyses are shown in Table 2. All the PMN–PT layers exhibit a density higher than 90% of the theoretical one after the sintering. We believe that the main reason for such a high density is that the green deposits are homogeneous, resulting from a well-dispersed, stable colloidal suspension with a small amount of organic phase and carefully chosen parameters for the deposition process.

The PMN–PT thick film sintered at 950 °C was 54 μm thick. With an increased sintering temperature the thickness of the layer decreases and the density slightly increases, indicating that the sintering process of the PMN–PT proceeds, at least to some extent. The thicknesses of the deposits prepared from the PMN–PT 2% PbO suspension were higher than the ones prepared from PMN–PT suspension. This is consistent with the result shown in Fig. 3. The mass of the deposit for a particular voltage and time is always higher for the PMN–PT 2% PbO suspension than for PMN–PT. As a consequence, a thicker structure is to be expected for deposits from the PMN–PT 2% PbO suspensions. Our results indicate that the PMN–PT 2% PbO layers are also denser than the PMN–PT ones after sintering at a particular temperature. Layers of PMN–PT 2% PbO some 67 and 56 μm thick with 94 and 95% of the theoretical density were obtained after sintering at 950 and 1100 °C, respectively.

Table 2
Dielectric properties of PMN–PT and PMN–PT 2% PbO sintered at 950 and 1100 °C for 2 h.

	T sintering (°C)	Thickness (μm)	Density (%)	T_m	ε @ 1 kHz	P_r (μC/cm^2)	E_c (kV/cm)
PMN–PT	950	54	90	170 °C	1,200	12	12
PMN–PT	1100	43	91	172 °C	9,550	16	7
PMN–PT 2% PbO	950	67	94	172 °C	13,500	15	7
PMN–PT 2% PbO	1100	56	95	172 °C	20,250	17	5

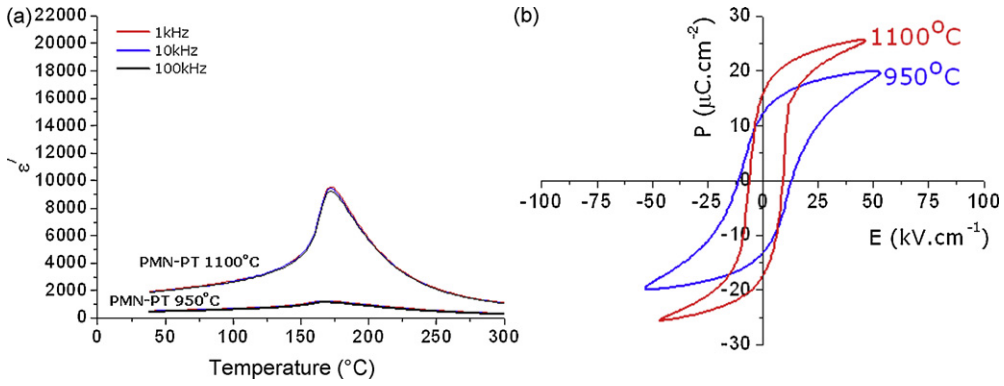

Fig. 7. PMN–PT sintered at 950 and 1100 °C for 2 h. (a) The temperature dependence of dielectric permittivity ε; (b) *P–E* curves.

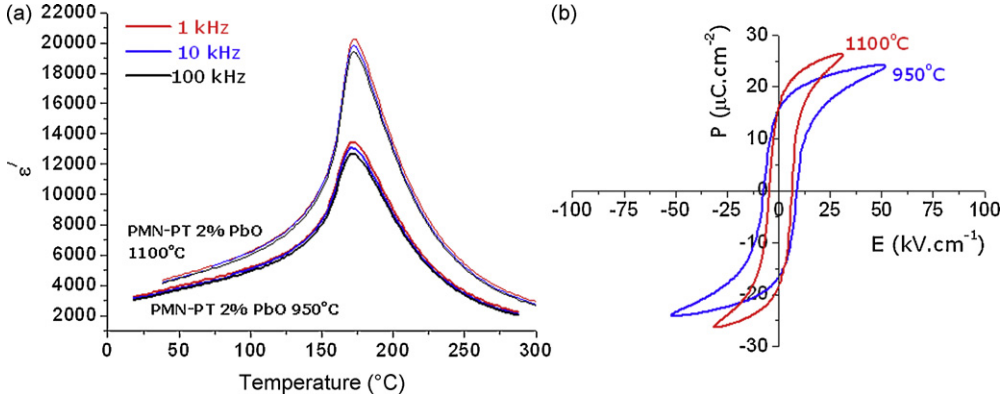

Fig. 8. PMN–PT 2% PbO sintered at 950 and 1100 °C for 2 h. (a) The temperature dependence of dielectric permittivity ε; (b) *P–E* curves.

The higher density of the PMN–PT 2% PbO thick films indicates that both the PbO and PMN–PT particles were deposited on the substrate during the electrophoretic deposition process. At the sintering temperature the excess PbO that is present between the PMN–PT grains melts and induces sintering in the presence of the liquid phase, which is well known from the literature.[12,13,23,24] Consequently, the PMN–PT 2% PbO layers are denser than the ones prepared from the PMN–PT suspension. The thick films prepared from the PMN–PT suspension consists of PMN–PT grains and do not contain any excess of PbO. As a result, sintering in the presence of a PbO liquid phase is not possible and does not apply to the PMN–PT grades.

3.4. Ferroelectric properties of thick film PMN–PT structures

The temperature dependences of the dielectric permittivity for the PMN–PT and PMN–PT 2% PbO sintered at 950 and 1100 °C are shown in Fig. 7a and 8a. The PMN–PT sintered at 950 °C shows a dielectric permittivity of 1200 at T_m and 1 kHz. When the sample is sintered at 1100 °C, the dielectric permittivity increases significantly and reaches a value of 9550 at T_m and 1 kHz. The remanent polarization increases from 12 to 16 μC/cm^2 and the coercive field decreases from 12 to 7 kV/cm for the samples sintered at 950 and 1100 °C, respectively. The PMN–PT 2% PbO sintered at 950 °C possesses a dielectric permittivity of 13,500 at T_m and 1 kHz, which is significantly higher than the value obtained for the PMN–PT sintered under identical conditions. The dielectric permittivity was even improved by sintering the PMN–PT 2% PbO at 1100 °C, reaching the highest value of 20,250 at T_m and 1 kHz. The remanent polarizations P_r of 15 and 17 μC/cm^2 and the coercive fields of 7 and 5 kV/cm were obtained for the samples sintered at 950 and 1100 °C.

The results indicate that higher values of the dielectric permittivity, higher remanent polarizations and lower coercive fields are obtained by increasing the sintering temperature. The functional properties of the PMN–PT thick films were improved significantly when we carried out the sintering in the presence of a liquid phase.

4. Summary

Single-phase, homogeneous, dense and crack-free PMN–PT thick films have been prepared by electrophoretic deposition followed by sintering. The mixture of a polyacrylate salt and an organic base provided good dispersion and surface charging of the PMN–PT particles in ethanol. The electrophoretic deposition of negatively charged PMN–PT particles was performed under a constant applied voltage of 10 V and a deposition time of 120 s on a Pt/PZT/Al_2O_3 substrate that acts as an anode. The deposits obtained from the PMN–PT and PMN–PT with PbO-excess suspensions were sintered at 950 and 1100 °C in a PbO-rich atmosphere. Within the detection limit of the XRD, no secondary phases could be identified in the perovskite coatings.

The density of all the PMN–PT thick films exceeds 90% of the theoretical density as a consequence of a well-dispersed, stable colloidal suspension with a small amount of organic phase, in addition to the optimised parameters used for the deposition and sintering process. The density of the PMN–PT film increases with the increasing sintering temperature and as a result of performing the sintering in the presence of a liquid phase. The highest functional response was obtained for a PMN–PT 2% PbO thick film sintered at 1100 °C for 2 h. The properties were as follows: a dielectric permittivity ε of 20,250 at 1 kHz at a T_m of 172 °C, a remanent polarization of 17 $\mu C/cm^2$ and a coercive field of 5 kV/cm.

Acknowledgements

The financial support of the Slovenian Research Agency and EU 6FP Network of Excellence MIND (NoE 515757-2) is gratefully acknowledged. Mrs. Marta Kozole and Mr. Silvo Drnovšek are thanked for their technical assistance.

References

1. Zhytomirsky I. Catodic electrodeposition of ceramic and organoceramic materials. Fundamental aspects. *Adv Colloid Interface Sci* 2002;**97**:279–317.
2. Harbach F, Nienburg H. Homogeneous functional ceramic components through electrophoretic deposition from stable colloidal suspensions. I. Basic concepts and application to zirconia. *J Eur Ceram Soc* 1998;**18**:675–83.
3. Deliormanli AM, Celik E, Polat M. The isoelectric point of lead magnesium niobate. *J Am Ceram Soc* 2007;**90**:3314–7.
4. Chen J, Fan H, Chen X, Fang P, Yang C, Qiu S. Fabrication of pyrochlore-free PMN–PT thick films by electrophoretic deposition. *J Alloys Compd* 2009;**471**:L51–3.
5. Chen J, Fan H, Ke S, Chen X, Yang C, Fang P. Relaxor behavior and dielectric properties of lead magnesium niobate–lead titanate thick films prepared by electrophoresis deposition. *J Alloys Compd* 2009;**478**: 853–7.
6. Reed JS. *Principles of Ceramics Processing*. 2nd ed. John Wiley & Sons; 1995.
7. Guldberg-Pedersen H, Bergström L. Stabilizing ceramic suspensions using anionic polyelectrolytes: adsorption kinetics and interparticle forces. *Acta Mater* 2000;**48**:4563–70.
8. Cesarano III J, Aksay IA, Bleier A. Stability of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolyte. *J Am Ceram Soc* 1988;**71**:250–5.
9. Sakar-Deliormanli A, Celik E, Polat M. Adsorption of anionic polyelectrolyte and comb polymers onto lead magnesium niobate. *Colloids Surf A: Physicochem Eng Aspects* 2007;**316**:202–9.
10. Popa AM, Vleugels J, Vermant J, Van der Biest O. Influence of ammonium salt of poly-metacrylic acid and butylamine addition on the viscosity and electrophoretic deposition behaviour of ethanol-based powder suspension. *Colloids Surf A: Physicochem Eng Aspects* 2005;**267**:74–8.
11. Popa AM, Vleugels J, Vermant J, Van der Biest O. Influence of surfactant addition sequence on the suspension properties and electrophoretic deposition behaviour of alumina and zirconia. *J Eur Ceram Soc* 2006;**16**:933–9.
12. Kuscer D, Skalar M, Holc J, Kosec M. Processing and properties of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ thick films. *J Eur Ceram Soc* 2009;**29**:105–13.
13. Kosec M, Holc J, Kuscer D, Drnovšek S. $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ thick films from mechanochemically synthesized powder. *J Eur Ceram Soc* 2007;**27**:3775–8.
14. Kosec M, Holc J, Malič B, Bobnar V. Processing of high performance lead lanthanum zirconate titanate thick films. *J Eur Ceram Soc* 1999;**19**:949–54.
15. Kuscer D, Korzekwa J, Kosec M, Skulski R. A- and B-compensated PLZT *x*/90/10: sintering and microstructural analysis. *J Eur Ceram Soc* 2007;**27**(16):4499–507.
16. Kuscer D, Holc J, Kosec M. Formation of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ using a high-energy process. *J Am Ceram Soc* 2007;**90**:29–35.
17. Kuscer D, Tchernychova Šturm E, Kovač J, Kosec M. Characterization of the amorphous phase and the nanosized crystallites in high-energy-milled lead–magnesium-niobate powder. *J Am Ceram Soc* 2009;**92**:1224–9.
18. PDF-ICDD. *PCPDFWin Version 2.2, June 2001*. International Centre for Diffraction Data; 2002.
19. Kumar Singh A, Pandey D. Evidence for M_B and M_C phases in the morphortopic phase boundary region of $(1-x)[Pb(Mg_{1/3}Nb_{2/3})O_3]$–$xPbTiO_3$: a Rietveld study. *Phys Rev B* 2003;**67**:064102-1–12.
20. Negishi H, Yamaji K, Sakai N, Horita T, Yanagishata H, Yokokawa H. Electrophoretic deposition of YSZ powders for solid oxide fuel cell. *J Mater Sci* 2004;**39**:833–8.
21. Hamaker HC. Formation of deposit by electrophoresis. *Trans Farad Soc* 1940:279–87.
22. Put S, Vleugels J, Van der Biest O. Gradient profile prediction in functionally graded materials processed by electrophoretic deposition. *Acta Mater* 2003;**51**:6303–17.
23. Snow GS. Fabrication of transparent electrooptic PLZT ceramics by atmosphere sintering. *J Am Ceram Soc* 1973;**56**:91–6.
24. Guha JP, Hong DJ, Anderson HU. Effect of excess PbO on the sintering characteristic and dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$-based ceramics. *J Am Ceram Soc* 1988;**71**:C-152–4.