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$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ thick films from mechanochemically synthesized powder

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Abstract

The phase composition, microstructure and electrical properties of thick-film structures based on $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ (PMN–PT) were studied. PMN–PT powder with 2 mol% of excess PbO was prepared by high-energy milling from the constituent oxides. A high yield of perovskite PMN–PT with nano-sized particles was obtained after the synthesis. A paste was prepared from the obtained powder, screen printed on platinised alumina substrates and sintered at 850, 900 and 950 °C. Single-phase PMN–PT thick-film structures without any pyrochlore phase were obtained after the sintering. The dense PMN–PT layers had good dielectric, piezoelectric and ferroelectric properties. The relative dielectric permittivity of 4100 and the peak value of 41,000 for the film sintered at 950 °C compare well with bulk ceramics sintered at much higher temperatures. The d_{33} value of the film was 170 pC/N. The obtained values for the dielectric properties demonstrate the good chemical homogeneity of material synthesized by high-energy milling.

Keywords: Films; Electron microscopy; Piezoelectric properties; Niobates; Perovskites

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN)–$PbTiO_3$ (PT)-based materials exhibit a high dielectric constant, high electrostrictive and piezoelectric properties and are suitable for applications in multilayer capacitors, actuators, sensors and electro-optical devices.[1] To downsize the final device, the active material must be miniaturised and integrated into the substrate. Screen-printing technology has been shown to be a successful method for forming an integrated film on a substrate, with the thickness ranging from a few micrometers to a few tens of micrometers.

To obtain acceptable dielectric and piezoelectric properties the active layer has to be chemically homogeneous without any undesirable phase, e.g., pyrochlore, and with a uniform microstructure. The main difficulty with thick-film processing is ensuring good adhesion as well as avoiding chemical reactions between the active layer and the substrate. To achieve these requirements, lowering the processing temperature is of great interest. Two approaches are commonly used, i.e., to use sub-micron-sized or nano-sized powder or/and to add a sintering aid. By using fine powder, the densification process can start at a lower temperature,[2,3] and as a result the reactivity between the thick film's components can be hindered. To improve the density of the active film various sintering aids such as $Li_2B_4O_7$[3] and Cu_2O–PbO[4] were added. However, these additives can reduce the functional response of the layer.[5] It is clear that the densification of the film is improved significantly in the presence of a PbO liquid phase.[6–9] Due to the low melting point and the high vapour pressure of PbO, it forms a liquid phase that improves the densification process, but with careful control of the atmosphere during the processing it can be removed from the active film.[6]

A room-temperature permittivity of 4000 was achieved for a $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ thick-film structure processed on alumina and silicon substrates from sub-micron powder.[3] The film on the silicon was prepared by using $Li_2B_4O_7$ as a sintering aid, and a peak value of 13,000 was obtained. For the film on alumina the peak value was 8200. The dielectric and ferroelectric properties of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ bulk ceramic prepared by hot pressing and annealing at 1150 °C are listed in Table 1.

The aim of our work was to process PMN–PT thick-film structures on a platinised alumina substrate from high-energy-milled nano-sized powder using screen-printing technology. The main emphasis was to process the thick-film structures at as low a temperature as possible, while still achieving acceptable microstructural properties and a good functional response in

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Table 1
Dielectric, ferroelectric and piezoelectric properties of PMN–PT thick films sintered at 850, 900 and 950 °C

T_{sint} (°C)	ε (1 kHz, at T_{room})	$tg\ \delta$ (1 kHz)	P_{r} (μC/cm^2)	E_{c} (kV/cm)	T_{m} (°C, 1 kHz)	ε (at T_{m}, 1 kHz)	d_{33} (pC/N)
850	760	0.05	8	25	175	1750	94
900	1100	0.04	11	21	163	10,165	140
950	4100	0.04	26	5.7	168	41,000	170
Thick film[3]	4000				120	8200	
Bulk	5229[18]	0.02[18]	12.3–33.1[17]	3.3–4.3[17]	169–190[17]; 160[18]	8160–41,720[17]; 36,000[18]	700[18]

Reported properties depend on thermal treatment of the sample.[17]

order that the material would be suitable for integration into miniaturised devices.

2. Experimental

For the experimental work we used 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).

A mixture of PbO, MgO, TiO_2 and Nb_2O_5 in the molar ratio corresponding to the stoichiometry of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ with 2 mol% of excess PbO (denoted PMN–PT) was high-energy milled in a planetary mill (Retsch, Model PM 400, Hann, Germany) for 64 h. A total of 200 g of powder was placed in the vial.

The rotational speed of the supporting disk was set to 300 rpm. Experimental details together with the properties of the powder are given in Refs. 10,12. The as-milled powder was heated to 700 °C for 2 h and analyzed using XRD. Sintering curves of the as-milled powder were recorded with a heating-stage microscope (Leitz Wetzlar, Germany) in the temperature range between 25 and 1300 °C at a heating rate of 10 °C/min in air.

The PMN–PT paste was prepared from high-energy-milled powder, fired at 700 °C, and an organic vehicle. The alumina substrates were prepared by slip casting from Alcoa A-16 and sintering at 1700 °C for 4 h. The platinum paste (Ferro 6412, Hanau, Germany) was screen printed on the Al_2O_3 substrate and fired at 1300 °C for 2 h. The PMN–PT paste was printed on the platinised Al_2O_3 substrate and pre-fired at 600 °C for 1 h. Samples were sintered at 850, 900 and 950 °C, respectively, for 2 h in a lead-oxide-rich atmosphere.

The X-ray powder-diffraction data for the powders and thick films 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[11] database.

A JEOL 5800 scanning electron microscope (SEM), equipped with a Tracor-Northern energy-dispersive system (EDS) was used for the overall microstructural analysis.

For the electrical measurements gold electrodes were sputtered onto the thick films. The values of the remanent polarisation and the coercive field were determined from ferroelectric hysteresis curves measured with an Aixact TF Analyser 2000. The real and the imaginary parts of the complex dielectric constant were measured with an HP 4284 A Precision LCR Meter. The samples were polarised at 150 °C. The piezoelectric piezo d_{33} constant was measured using the Berlincourt method (Take control PM10).

3. Results and discussion

In order to determine the sintering interval for the PMN–PT thick films, the sintering behaviour of high-energy-milled PMN–PT nano-sized powder was studied. The sintering curve of the PMN–PT shown in Fig. 1 indicates that the powder starts to sinter at 800 °C and reaches a final linear shrinkage of 20% at 1300 °C in air. The mechanically activated powder contains a high yield of perovskite PMN–PT and a trace amount of pyrochlore phase. Besides crystalline phases it also contains approximately 30 wt.% of amorphous phase that crystallises at temperatures higher than 500 °C into the perovskite phase, as reported in Refs. 10,12.

The PMN–PT thick films were prepared from high-energy-milled powder fired at 700 °C. Cross-sectional SEM images of the PMN–PT thick films on the platinised Al_2O_3 substrates fired at 850, 900 and 950 °C are shown in Fig. 2a–c, respectively. The thickness of the film decreases with increasing temperature and ranges between 60 and 35 μm at 850 and 950 °C, respectively. The microstructure of the films shows a uniform particle size and pore size distribution. At 850 °C the film is fine-grained. From the microstructure it was estimated that the grain size of the PMN–PT is below one micrometer. According to the sintering curve of the PMN–PT containing an excess of 2 mol% of PbO (Fig. 1) the powder starts to densify at 800 °C. It is known

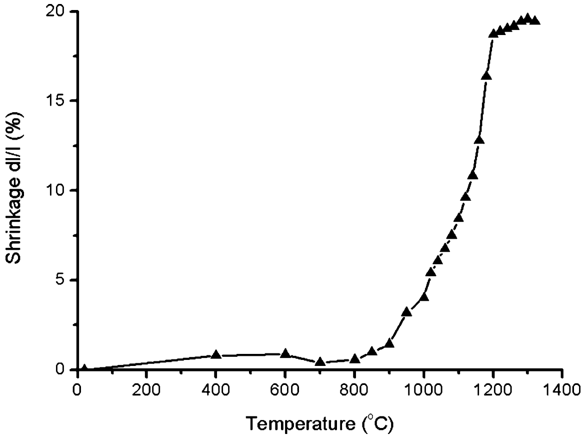

Fig. 1. Sintering curve of as-milled PMN–PT powder from 20 to 1350 °C in air.

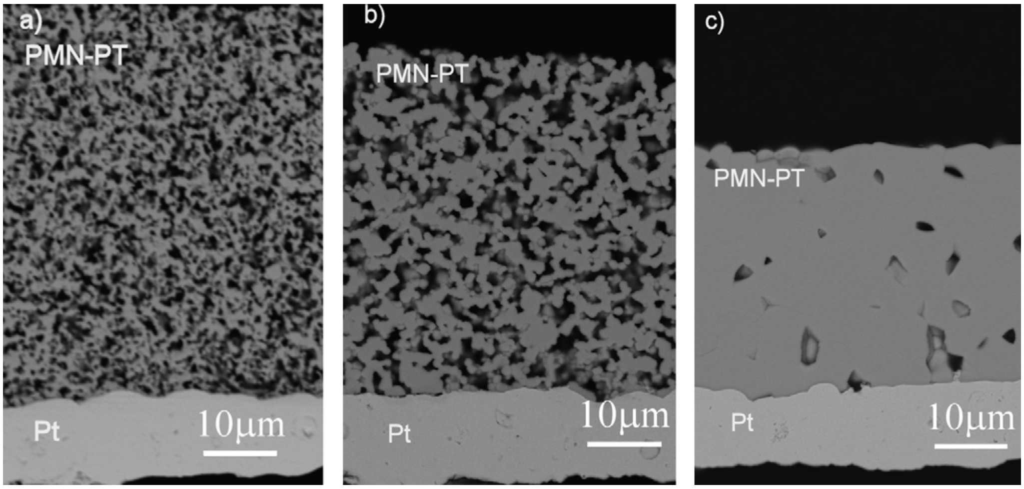

Fig. 2. SEM image of PMN–PT on Pt/Al_2O_3 substrate fired at (a) 850 °C, (b) 900 °C and (c) 950 °C for 2 h. Pt: platinum and PMN–PT: $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$.

that in the presence of liquid PbO the densification process is promoted.[6,9] Since PbO melts at 888 °C,[13] liquid-phase sintering would be expected in the samples sintered at 900 and 950 °C. With increasing temperature the grain size increases, as can be seen from the microstructures in Fig. 2. After sintering at 900 °C the estimated grain size is about 2 μm, and at 950 °C the grain size increases significantly.

X-ray powder diffractograms of the PMN–PT thick film sintered at 850, 900 and 950 °C are shown in Fig. 3. In contrast to the PMN–PT powder, where a pseudo-cubic structure with a lattice parameter of $a = 0.40184 \pm 0.00006$ nm was obtained after firing at 850, 900 and 950 °C, the structural change from pseudo-cubic to a tetragonal structure was observed in the PMN–PT thick films. The XRD pattern of the PMN–PT thick film sintered at 850 °C is similar to that of the PMN–PT powder and was indexed on the basis of a pseudo-cubic structure with $a = 0.40184 \pm 0.00006$ nm. The thick film sintered at 950 °C was indexed on the basis of a tetragonal structure with $a = 0.40034 \pm 0.00003$ and $c = 0.40446 \pm 0.00003$ nm. The calculated c/a ratio was 1.010. The calculated lattice parameters agree well with the reported values for 0.65PMN–0.35PT bulk ceramic.[14] A structural change of the pseudo-cubic to the tetragonal 0.7PMN–0.3PT structure was also observed by Zhang et al.,[15] who reported that the change is caused by the loss of PbO. The pseudo-cubic-to-tetragonal change in the thick-film PMN–PT may also occur as a result of PbO loss, which can take place during the sintering process. At higher temperatures the PbO vapour pressure is higher and therefore PbO can evaporate and/or diffuse from the film into the substrate. The SEM/EDS analysis of the PMN–PT structure sintered at 950 °C showed that the alumina substrate contained lead-rich phases, as was previously observed in lead-based perovskite thick films.[6,16] This indicates that the PbO can diffuse from the active PMN–PT film into the Al_2O_3 substrate.

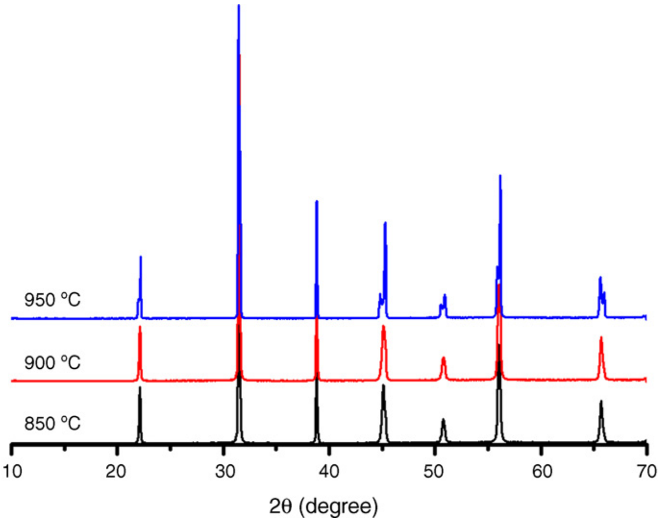

Fig. 3. X-ray powder diffractogram of PMN–PT thick films sintered at 850, 900 and 950 °C.

The functional properties of the PMN–PT sintered film are shown in Table 1. An outstanding functional response was obtained for the PMN–PT film sintered at 950 °C that shows ferroelectric to paraelectric transition with transition temperature T_m of 168 °C (Fig. 4). The remanent polarisation of 26 $\mu C/cm^2$ and the coercive field of 5.7 kV/cm match the values reported for PMN–PT bulk ceramic.[17] The piezoelectric constant d_{33} was 170 pC/N for the film sintered at 950 °C. The room-temperature relative dielectric permittivity of 4100 is comparable to the reported values for bulk samples and thick films on alumina substrates.[3,18] The transition temperature and the maximum of the relative dielectric permittivity show a very sharp ε–T behaviour and a weak T_m frequency dependence, typical for a normal ferroelectric material (Fig. 4). The sharp transition of the relative dielectric permittivity at T_m indicates that the film sintered at 950 °C is chemically homogenous.[17] The ε peak value of 41,000, achieved on the PMN–PT thick-film structure, is comparable with the highest reported values for PMN–PT bulk ceramics.[17,18] The relative dielectric permittivity of the films sintered at 850 and 900 °C is lower. The reasons are numerous but the most possible are the low density of the film and low chemical homogeneity.

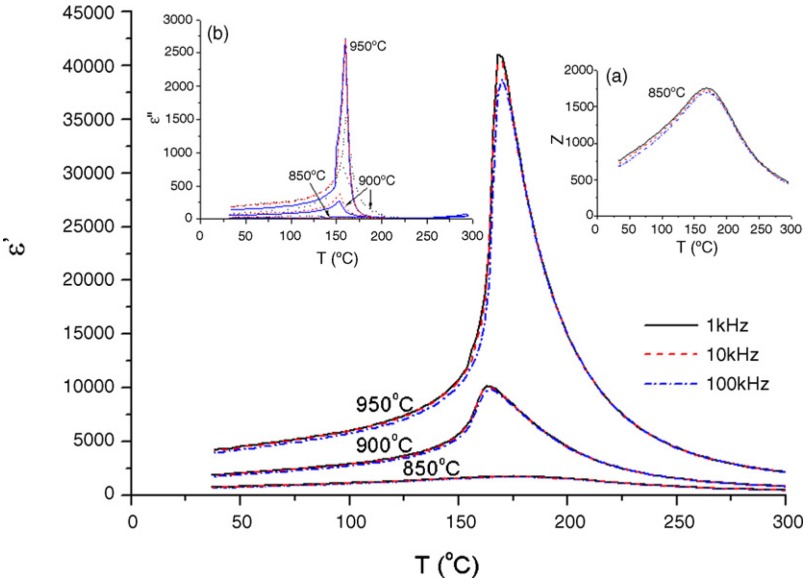

Fig. 4. The real part of the dielectric permittivity ε' of PMN–PT thick films sintered at 850, 900 and 950 °C as a function of temperature. The real part of the dielectric permittivity ε' of the PMN–PT film sintered at 850 °C is shown as an inset (a). The imaginary part of the dielectric permitivity ε'' for the PMN–PT thick films sintered at 850, 900 and 950 °C at 1, 10 and 100 kHz is shown in inset (b).

4. Summary

Thick-film $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ structures on platinised alumina substrates were prepared from high-energy-milled nano-sized powder using screen-printing technology and sintering at 850, 900 and 950 °C. Using nano-sized powder together with the addition of 2 mol% of excess PbO resulted in a homogeneous, single-phase and relatively dense microstructure. Outstanding functional properties for the PMN–PT thick film were obtained after sintering at 950 °C. The room-temperature relative dielectric permittivity of 4100, the dielectric losses of 0.04, the remanent polarisation of 26 μC/cm^2, the coercive field of 5.7 kV/cm, the T_m of 168 °C, the permittivity at T_m of 41,000 and the d_{33} of 170 pC/N are comparable to values obtained for PMN–PT bulk ceramics. The obtained thick-film PMN–PT structures are possible candidates for the production of micro-piezoelectric devices.

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