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Electrophoretic deposition and properties of strontium-doped sodium potassium niobate thick films

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ABSTRACT

We have processed strontium-modified potassium sodium niobate (KNNSr) piezoelectric thick films on metalized alumina by electrophoretic deposition and sintering for energy-harvesting applications. The deposition yield, the electric field in the close vicinity of the planar working electrode (calculated with a finite-element method) and the thickness profiles of the as-deposited layers were examined for ethanol-based suspensions with different conductivities, deposition times, inter-electrode distances and sizes of the counter electrode. Uniformly thick and defect-free, as-deposited KNNSr layers were processed from a suspension with a conductivity of 21.2 $\mu\text{S}/\text{cm}$, deposited for 90 s, for an inter-electrode distance of 3 mm and a diameter of the counter electrode similar to the sample's dimensions. KNNSr layers sintered at 1100 °C with a thickness of 30 μm and a relative density of 75% exhibited a dielectric permittivity of 325, dielectric losses of 0.04 at 10 kHz and room temperature, and a d_{33} coefficient of 60 pC/N.

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1. Introduction

An energy harvester is a device that generates electrical energy from ambient-available energy sources to provide an uninterrupted power supply for various devices, such as wireless, self-powered microsystems and macroscale devices [1–3]. A piezoelectric energy harvester (PEH) exploits vibrations, pressure and stress-strain energy and converts them to electrical energy using the capability of the piezoelectric material to produce an electrical charge when subjected to a mechanical load [4]. The properties of piezoelectric materials dictate the energy-convergence efficiency η of the material, which increases with increasing values of the electromechanical coupling factor k_{ij} and the mechanical quality factor Q_m . In addition, the electrical energy produced by a piezoelectric energy harvester is proportional to the piezoelectric strain coefficient d_{ij} , the piezoelectric voltage coefficient g_{ij} and the applied force [4]. Accordingly, the efficiency of the PEH depends on both the properties of the piezoelectric material and the architecture of the device [3,4].

The most common PEH configuration is a cantilever. In such a configuration the piezoelectric material is deposited on a substrate forming a unimorph-, bimorph- or multilayer-structured PEH [3]. The most common process for fabricating a unimorph or bimorph PEH initiates from a bulk piezoelectric ceramic that is diced and thinned to the required dimensions and subsequently attached to the substrate with glue [4,5]. However, the difficulty of handling thin, miniaturised ceramic pieces during the preparation and assembly steps makes this process unpractical, rather time consuming and thus economically unsustainable. In contrast, thick-film technology offers the advantage of integrating tens-of-micrometres layers directly onto the substrate and therefore eliminates the difficulty of handling the thin, bulk ceramic [6]. A technology for the relatively fast processing of thick films on complex-shape substrates is electrophoretic deposition (EPD). This process is based on the mobility and subsequent deposition of charged particles dispersed in a solvent onto an oppositely charged, electrically conductive electrode induced by the application of a DC electric field between two electrodes. The deposit yield depends on the properties of the suspension, i.e., the electrophoretic mobility of the particles and the solids load, as well as on the deposition conditions, i.e., the local electric field strength, the electrode area, and the deposition time. A detailed description of the EPD process can be found elsewhere [7–9].

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Polyelectrolytes based on polyacrylic acid (PAA) have been widely used for dispersing metal oxide particles in aqueous media [10–12]. The interactions between the polyelectrolyte and the metal oxide particles depend on the chemical and physical properties of the particle's surface, the type and conformation of the polyelectrolyte and the solvent's properties [13,14]. Poly(acrylic acid-co-maleic) acid (PAM), with a larger number of carboxyl groups compared to PAA, was reported to be an effective additive for the stabilization of lead zirconate titanate and barium titanate particles in water at alkaline pH [15,16]. The deprotonation of the carboxyl groups in water depends on the pH of the medium. At a pH lower than 4 the carboxyl groups are protonated ($-\text{COOH}$) and the PAM is in coil conformation [15,17]. By increasing the pH the $-\text{COOH}$ groups start to deprotonate, forming an carboxylate anion ($-\text{COO}^-$), and at a pH higher than 8 the carboxyl groups are completely deprotonated [15]. In neutral and alkaline pHs the PAM with partly or completely deprotonated carboxyl groups adsorbs on the metal oxide particles and provides the electrosteric stabilization of metal oxides in the media. Carboxyl-group-containing polyelectrolytes have been reported to be effective additives for the stabilization of metal oxide particles in alcohols, with the addition of an organic base, such as *n*-butylamine [18–20].

The quality of the as-deposited layers prepared by EPD depends on the deposition parameters. In particular, the thickness uniformity of the as-deposited layer is related to the uniformity of the electric field in the close vicinity of the working electrode. It was reported that the electric field between the two planar electrodes is homogeneous in the central region of the electrode, but non-homogeneous and stronger at its edges [21]. Consequently, the thickness of the as-deposited layer was larger at the edges of the electrodes, especially for short deposition times [22,23]. In addition, it was shown that the uniformity of the electric field depends on the inter-electrode distance and the diameter of the counter electrode [24].

Environmentally benign, lead-free piezoelectric materials have been studied extensively as a result of European Union regulations that restrict the use of certain hazardous materials, including lead-based compositions in electronic devices and electrical equipment (as summarised in [25]). Potassium sodium niobate with the nominal composition $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (denoted KNN), which has been recognised as a potential substitute for lead-based piezoelectrics, is characterised by a moderate piezoelectric response (dielectric permittivity ~ 500 , $d_{33} \sim 80$ pC/N, $k_p \sim 0.4$), but temperature-stable piezoelectric properties and a relatively high Q_m , i.e., 240 [26,27]. However, it is difficult to obtain a single-phase, dense KNN ceramic with a reproducible microstructure. The hygroscopic nature of raw materials, in particular carbonates, and the volatilisation of alkalis during high-temperature curing, frequently result in a deviation of the stoichiometry of the final compound, the formation of undesirable secondary phases and the segregation of sodium and potassium ions, which deteriorate the functional properties of the ceramic [28–30]. The limitation also presents grain coarsening in the initial stage of the sintering and a narrow temperature range for the sintering [31,32].

In our previous work we showed that the modification of KNN with up to 2% of Sr^{2+} improves the density of the ceramic, significantly reduces the grain size and hinders the formation of the secondary phases [27,33,34]. The addition of up to 0.5% of Sr^{2+} also, to some extent, increases the dielectric permittivity and piezoelectric d_{33} coefficient as well as decreases the dielectric losses $\tan \delta$ [33,34]. At Sr^{2+} levels higher than 2%, the secondary phase was formed [33,35]. Based on the aforementioned characteristics of the Sr-modified KNN, we used the composition with 0.5% of Sr for the processing of thick films for PEH applications.

Despite the great interest in realising lead-free piezoelectric thick films, reports on the processing of KNN-based thick films

by EPD are rare. An example is KNN thick films prepared on platinum foil by EPD from acetone- and water-based suspensions and subsequent sintering [36,37]. The micrometer-sized powder was stabilised in acetone using iodine and triethanolamine (TEA), and in water by the addition of sodium dodecyl sulphate (SDS). Regardless of the extremely low zeta-potential of KNN stabilised in acetone with TEA, i.e., 1.3 mV, the as-deposited layers were uniform under optimised deposition conditions. After sintering at 1100°C the thick films crystallised in a perovskite structure, but also contained a small amount of polyniobate secondary phase. The thick films exhibited a dielectric permittivity of 393 and $\tan \delta$ of 7% at 1 MHz and room temperature [36]. KNN stabilised in water by sodium dodecyl sulfate (SDS) possessed a zeta-potential of -76 mV. The resulting as-deposited layers had a relative density of 65%, were uniform and crack-free. After sintering at 1100°C , the layers were thinner, i.e., $10\ \mu\text{m}$, and contained, in addition to the perovskite phase, the polyniobate phase. The authors suspected that the secondary phase may be formed either due to the dissolution of KNN in the solvents or due to the volatilisation of Na^+ during the sintering. The water-derived KNN thick films had a dielectric permittivity of 495 and a $\tan \delta$ of 8% at 1 MHz and room temperature [37]. The piezoelectric d_{33} coefficients of the films sintered under identical conditions, i.e., 1100°C , were 68 and 40 pC/N for films derived from water- and acetone-based suspensions, respectively. The dielectric permittivity of the thick films was comparable to that of the bulk ceramic with an identical nominal composition, but sintered at a higher temperature, i.e., 1170 and 1200°C , while the dielectric losses were higher and d_{33} coefficient was slightly lower, presumably due to the low relative density of the thick films compared to the bulk ceramic [29,37].

Here, the processing and characterisation of Sr-modified KNN thick films with the nominal composition $(\text{K}_{0.5}\text{Na}_{0.5})_{0.99}\text{Sr}_{0.005}\text{NbO}_3$ (KNNsSr) on platinised alumina substrates produced by EPD and subsequent sintering are reported. In accordance with our targeted application, we focused the work on processing crack-free and thickness-uniform, as-deposited layers. For this purpose, we first studied the properties of the powder and the suspension, i.e., the zeta-potential and the electrical conductivity, on the morphology of the as-deposited layers and on the deposition yield. In the second step, the influence of the deposition conditions, i.e., typically the distance between the electrodes and the size of the counter electrode, were studied to reach thickness-uniform, as-deposited layers. Finally, the processed layers under optimal conditions were sintered using two different conditions for the first evaluations. Dielectric and piezoelectric characterizations of the KNNsSr thick films were performed and compared to results already published in the literature.

2. Experimental procedure

Powder with the nominal composition $(\text{K}_{0.5}\text{Na}_{0.5})_{0.99}\text{Sr}_{0.005}\text{NbO}_3$ (denoted KNNsSr) was prepared by solid-state synthesis from K_2CO_3 (anhydrous, 99.9+ %, ChemPur, Germany), Na_2CO_3 (anhydrous, 99.9+ %, ChemPur, Germany), SrCO_3 (99.994%, Alfa Aesar, Germany) and monoclinic Nb_2O_5 (99.9985%, Alfa Aesar, Germany). The powder compacts were calcined at 800°C for 4 h and re-calcined at 750°C for 4 h with an intermediate milling. A detailed description of the synthesis is given elsewhere [35].

We prepared solutions of poly(acrylic acid-co-maleic acid) ($(\text{CH}_2-\text{CH}(\text{COOH})_x-\text{CH}(\text{COOH}))_y$, PAM, Mw 3.000, 50 wt% water solution, Sigma Aldrich, Germany) and *n*-butylamine ($\text{C}_4\text{H}_9-\text{NH}_2$, BA, Alfa Aesar, Germany) in ethanol (EtOH, anhydrous, Carlo Ebra, Italy) with concentrations of 1.13, 2.26 and

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