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Mask-Less Direct-Writing Deposition of Lead-Free Piezoelectric Films for Microsystems

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Abstract

Piezoelectric films fabricated with lead-free piezoelectric inks by means of a mask-less Direct-Writing (DW) technique are presented. A lead-free piezoelectric material, $K_{0.5}Na_{0.5}NbO_{3-\delta}$ (KNN), has been produced via Solid State Reaction (SSR) and Molten Citrate (MC) route in order to improve the microstructural properties of powders. The slurry composition and rheology have been optimized in order to obtain inks with physical properties compatible with the DW technique and layers with enhanced mechanical and piezoelectric properties. Experimental results obtained with pellets and films deposited on alumina substrates demonstrate the piezoelectric properties of the fabricated devices. The developed direct-writing technique will be implemented for the realization of precise patterns of piezoelectric sensors or actuators inside microsystems, without the requirement of manufacture expensive masks.

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Keywords: Mask-less direct-writing process; lead-free piezoelectric material; microsystems.

1. Introduction

Recently, there has been growing interest in Direct-Writing (DW) methods for the manufacturing of sensors and actuators, due to versatility and relatively high thickness of the deposited films (1-100 μm) [1]. Among different

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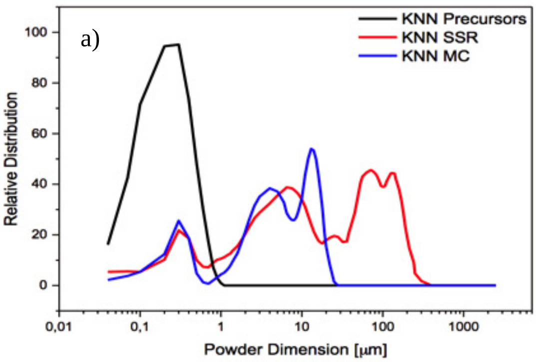
piezoelectric materials, KNN is nowadays one of the most important alternatives to PZT. During last years, the intensification of the importance about this class of compounds has been mainly drawn by the increasing of the environmental awareness, resulted in the approval of Restriction of Hazardous Substances (RoHS) [2] and Waste Electrical and Electronic Equipment (WEEE) [3] UE directives in 2003. In the following years, many other governments passed similar requirement restrictions on toxic elements and compounds, including lead for electronics. Thus, in the last decade, the development of an alternative to PZT led to an intensive research on KNN compounds, due to adequate Curie temperature and large d_{33}, nevertheless still far from PZT performance and its replacement in the market [4].

2. Preparation and deposition of lead-free piezoelectric films

The solid solution of $KNbO_3$-$NaNbO_3$ (KNN) has been synthesized through two different techniques: Solid State Reaction (KNN-SSR) and Molten Citrate (KNN-MC) route, since the microstructure of the powders is a key parameter to investigate for the final material properties. The powders morphology and dimension strongly influence the packing efficiency, leading to the possibility to increase the density of the sample produced from different powders of the same material. The desired pure single-phase compound has been produced with both the preparation routes, confirmed by XRD analysis, presenting much smaller particle dimension for the KNN-MC, as reported by the results of the granulometry analysis, shown in Fig. 1a. Both different KNN batches have been fully characterized chemically and structurally by several techniques (XRD, TGA/DTA/DSC, SEM, TEM, Rietveld and ICP analysis) and they have been used for the production of inks for DW deposition.

An investigation on the crystal lattice has been carried out on accurate XRD patterns, using Rietveld routine with GSAS software [5]. The results revealed that KNN crystallizes in an orthorhombic lattice with the space group *Amm2* (n° 38). The structure has been also investigated with the group representation theory, using the symmetry-adapted mode description of distorted structures [6], in order to evaluate the ongoing deformation of the crystal structure with the temperature increase. This increase of the deformation in the orthorhombic lattice continues up to the temperature of the phase transition (at about 194°C from DSC analysis). At this first phase transition (from Orthorhombic to Tetragonal), the compound should present the highest d_{33}, according to literature [7], due to the maximum difference between the lengths of the three couple of Nb-O bonds in the distorted Octahedral NbO_6 structures.

The slurry composition has been optimized through sedimentation and rheology measurements, testing several compounds as media carrier of the ink, such as PEG400, PEG1500, PEG4000 and Glycerol mixed with different ratios of water and powders in order to avoid the hollow needle occlusion during the deposition process. The optimal ink composition for DW process resulted in a trade-off between stability, powder content and viscosity, which is required below 0.4 Pa·s to ensure the DW deposition (Fig. 1b). The optimal ink results in the following composition: KNN-MC:Glycerol:Water (30:61:9 wt. % ratios).



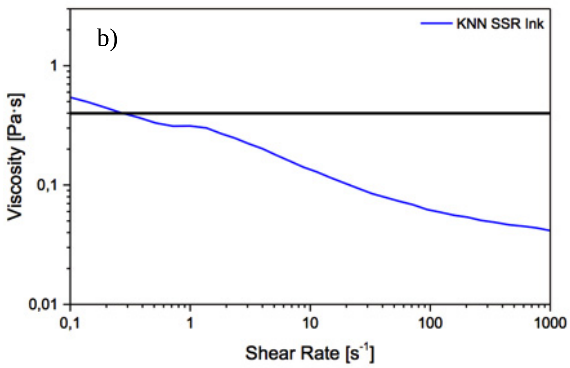


Fig. 1. (a) Relative distribution of particles of KNN precursors (Black Line), KNN-SSR (Red Line) and KNN-MC (Blue Line) versus powder dimension. (b) Viscosity of KNN-SSR ink versus applied shear rate (b); black line represents the maximum value allowed by Microplotter

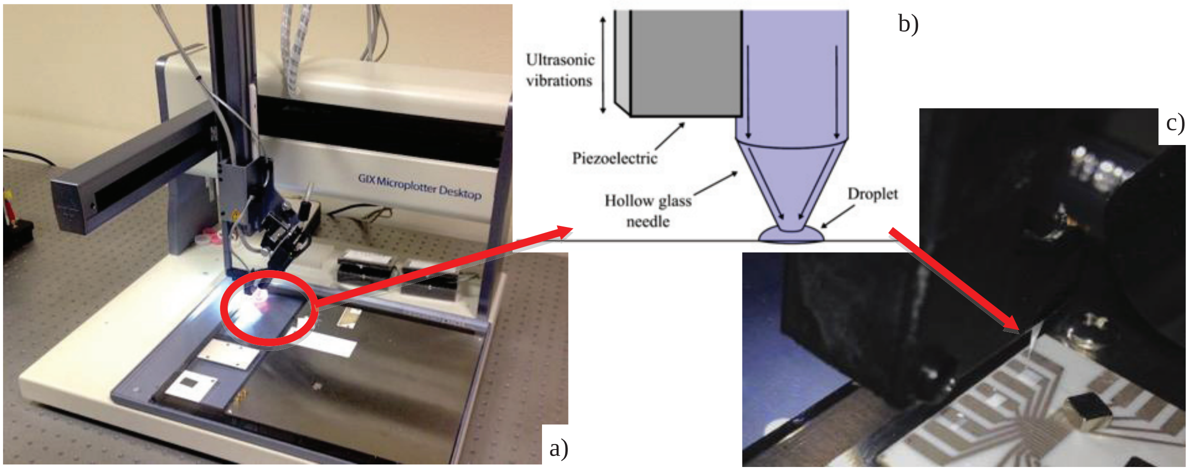


Fig. 2. (a) Equipment used for deposition of lead-free piezoelectric films (Sonoplot GIX Microplotter). (b) Schematic view of the direct-writing deposition technique. (c) Enlarged view of the hollow glass needle located over the substrate on which piezoelectric films are deposited.

The mask-less deposition of KNN ink has been carried out using the printing system Sonoplot Gix Microplotter, as show in Fig. 2a. The Microplotter directly dispenses a continuous flow creating precise patterns onto the substrate. The ink is loaded by capillary forces into a hollow glass needle and is ejected by ultrasonic vibrations, as reported in the schematic sketch of Fig. 2b and Fig. 2c. The contact between the drop meniscus and the substrate promotes the droplet detachment and the achievement of precise patterns. The process has a nominal resolution around 30 µm.

3. Experimental results

The piezoelectric ink has been dispensed on alumina substrate, as shown in Fig. 3a. Fig. 3b shows the film sample at the end of the deposition process, while Fig. 3c and Fig. 3d show the film sample after the sintering process (1000°C for 4 h) and after the deposition of the top electrode realized with a silver-based ink (DuPont 5000), respectively.

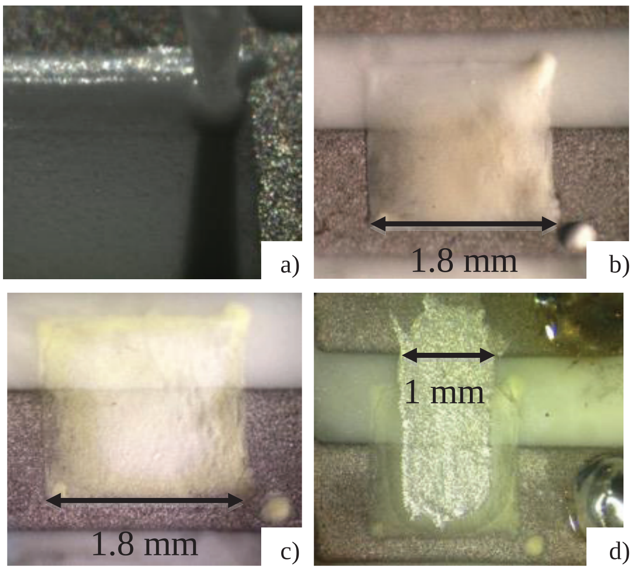


Fig. 3. (a) Film dispensed by ultrasonic direct writing on alumina substrate. (b) Film sample at the end of deposition process, (c) after sintering process and (d) after deposition of the top electrode.

The piezoelectric film has thickness of about 25 µm and has been poled with an applied electric field of 2MV/m at 120°C for 15 min. Fig. 4a shows the output voltage of the fabricated piezoelectric film measured using a high-impedance-input amplifier obtained under mechanical impulse excitation. The obtained results demonstrate the piezoelectric properties of the sample, as expected. The relative dielectric permittivity $\varepsilon_{\text{r-film}}$ was calculated from the measured capacitance C_{film}=24.3 pF and the physical dimensions, obtaining a value of about 92. Piezoelectric coefficients are currently being determined. As a further investigation, piezoelectric pellets have been realized by means of a manual hydraulic press. Fig. 4b shows the measured admittance spectrum of a 1-mm-thick and 13-mm-diameter pellet. The mechanical resonant frequency is at about 233 kHz, according to thickness resonance, while the calculated $\varepsilon_{\text{r-pellet}}$ results 107.

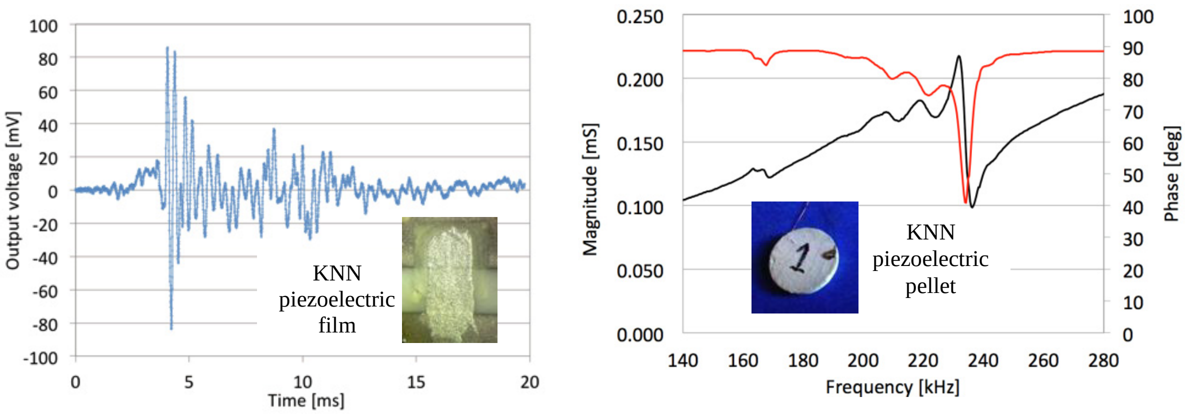


Fig. 4. (a) Measured output voltage of the fabricated 25-µm-thick piezoelectric film (shown in the insert) obtained under mechanical impulse excitation. (b) Measured admittance spectrum (magnitude and phase around resonance) of the 1-mm-thick fabricated piezoelectric pellet (shown in the insert).

4. Conclusions

A lead-free piezoelectric KNN material has been produced and chemically and structurally characterized. An optimized printable KNN ink has been obtained and deposited onto alumina substrates by mask-less direct-writing deposition. The fabricated films have been experimentally characterized to investigate their piezoelectric properties. The promising results demonstrate that DW techniques are a viable path to dispense lead-free piezoelectric materials in microsystems to realize sensors or actuators.

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