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Lead-Free Piezoelectric Vibration Energy Harvesters: Spark Plasma Sintered KNN compared with commercial KNN

Grégoire Forges[1,3], Nadia Bencharef [1,2], U-Chan Chung[2], Catherine Elissalde[2], David Gibus[3], Hélène Debéda[1]
[1]Univ. Bordeaux, CNRS, Bordeaux INP, IMS, UMR 5218 F-33405 Talence Cedex, France,
[2]Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France
[3]SYMME, Univ. Savoie Mont Blanc, F74000 Annecy, France
gregoire.forges@univ-smb.fr

Summary:

This work presents the use of lead-free piezoelectric material, pure KNN sintered by spark plasma sintering, for applications in vibration energy harvesting. KNN ceramics of dimensions 1 × 2 × 8 mm3 were densified at 1000°C and thinned to 0.5mm before electromechanical characterizations. The deduced parameters were used for the design of piezoelectric bimorph cantilever. A power of 115 µW at 1m/s² and a normalized power of $6.75\,\mu\mathrm{W.g^{-2}.mm^{-3}}$ are expected from FEM simulations. Such results are similar as those of commercial KNN ceramics, showing the potentialities of the process.

Keywords: Piezoelectric cantilever, SPS, KNN, FEM

Introduction

Considering the piezoelectric material in piezoelectric vibration energy harvesters (VEH), the community is looking for alternatives to lead-based perovskites. Lead-free piezoelectric perovskites, like (K,Na)NbO3 (KNN), are not only promising in both film or ceramic form but also challenging in the context of VEH [1]. Also, to reduce the cost of Silicon cantilevers a focus on the replacement of the Si substrate by metallic or polymer substrate [1-3] is done and thicker films (>10µm) may also help to maximize powered energy. However, the thermal budget of processes in literature is quite high with a firing step of hours at 900°C for example [4]. Hence, an original processing route combining screen-printing technology with Spark Plasma Sintering (SPS) process allowing sintering at lower temperature for short periods of time [5]. Here, the objective is to use pure KNN commercial nanoparticles to efficiently sinter bulk ceramic by SPS, before moving to the screen-printing/SPS combination to sinter a KNN screen-printed thick film printed on a StSt. For this process, controlling grains size and their distribution after SPS sintering will be the key to achieve characterizations similar than those of commercial KNN. After SPS sintering of the KNN, the electromechanical characterizations led on the fabricated KNN ceramics will be used to conduct FEM modelling and predict the harvested energy for bimorph cantilevers integrating KNN thinned ceramics.

Ceramic Process

Two dense (98 %) pellets of diameter 10 mm and 1 mm (D1) and 2 mm (D2) thick, were produced from a commercial KNN (K0.5Na0.5NbO3) nanopowder. The SPS equipment is Syntex Dr. Sinter Lab Model SPS-515S (Fig.1). The sintering process was led under vacuum at 1000°C for 15 min, with a pressure of 100 MPa and a heating rate of 100°C/min. Following sintering, an annealing treatment 2 hours at 1000°C was carried out to recover the oxygen stoichiometry [6]. The two pellets were initially coated with a thin layer of sputtered gold, then poled and characterized before being sectioned into bars (B1 and B2). Dimensions of 1 × 2 × 8 mm3 were prepared using a wire saw and subsequently polished to achieve a final thickness of 0.5 mm. As illustrated in Fig. 2, the bars were cut in two different orientations to assess the influence of the electric field direction during poling versus the pressure applied during SPS sintering, on the electromechanical properties. Subsequently, the bars underwent the same processing steps as the pellets, including metallization, poling, and characterization. The dielectric properties were led using a HP-4194 impedance/gain-phase analyzer. Poling was performed at room temperature in a silicone oil bath under an electric field of 3 kV/mm for 5 min. The piezoelectric coefficient d_{33} was then measured using a Berlincourt-type piezometer (frequency: 110 Hz, applied force: 0.25 N). Following sample preparation, structural and microstructural characterizations were performed. The X-ray diffraction pattern confirms an orthorhombic perovskite structure with no detectable secondary phases. At the microstructural level, the grains exhibit a cubic morphology with an average size of approximately 10µm (Fig. 3). Table I summarizes the values from dielectric and piezoelectric characterization for each configuration. After cutting, a difference was observed between the properties of the ceramic bars and the original disks. Dielectric loss increased by 2 to 6% and the d_{33} value decreased. This degradation may be attributed to mechanical stresses introduced during the cutting process, which can generate surface defects and cause partial depolarization of the already-poled ceramics. The effect is particularly pronounced in the 2 mm samples (B2), where the larger surface area exposed to mechanical stress leads to greater losses and more significant depolarization.

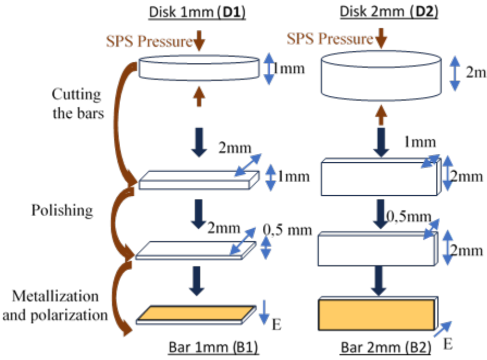

Fig.2 Ceramic process from SPS pellets to bars

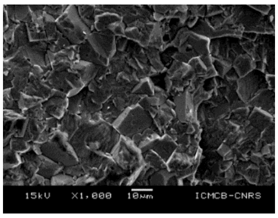

Fig.3 Scanning electron microscopy of the SPS ceramic fired at 1000°C

Tab 1: Dielectric and piezoelectric coefficients

	Disks		*Bars*	
	D_1	D_2	B_1	B_2
ε_r (1kHz, 25°C)	*380*		*350*	*400*
Dielectric losses (1kHz, 25°C)	*2 %*		*5 %*	*6 %*
d_{33} (pC/N)	*110*		*100*	*70*

31-Mode Characterization of bars

The KNN bars (B1) were assessed by impedance analysis to study the 31 piezoelectric mode, that is exploited in cantilevers. Mechanical and electrical material parameters were extrapolated using method from [7] (Tab. 2).

Tab. 2: Characteristics of assessed KNN bars

$f_0\,(kHz)$	k^2	Q_m	C_0 (pF)	$s_{11}^E(m^2.N^{-1})$	$d_{31}(pC.N^{-1})$	ϵ_{33}
343	0,048	133	57	$7{,}69.10^{-12}$	-35	324

Finite Elements Modeling

FEM on COMSOL Multiphysics was conducted to investigate the performance of KNN bars for energy harvesting in a bimorph cantilever with a steel substrate. The prototype dimensions are given in Tab. 3 and the harvested power is represented in fig.4. At 302 Hz, the power is 115 µW as shown on fig. 6. The normalized power to the acceleration and volume is $6.75\ \mu\mathrm{W.g^{-2}.mm^{-3}}$. When compared to industrial LF02B KNN [9], which is, commonly, not pure KNN with doping elements [9], the delivered power is comparable (Fig. 4). The resistive load for the LF02B was set to $940\ \mathrm{k\Omega}$ to achieve optimal power output.

Tab. 3: Geometric parameters and optimal resistive load

Length	**Width**	**Sub thick.**	**Piezo thick.**	**R_{Load}**	**Volume**
7,9 mm	1,95 mm	0,6 mm	*0,6 mm*	3,56 MΩ	1,64 cm^3

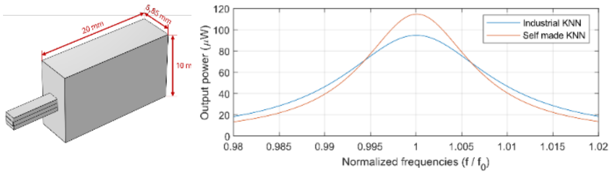

Fig. 4. Left : Prototype investigated in finite element simulation, Right : Harvested power for a pure optimal resistive load under the resonance frequency and an acceleration of $1\mathrm{m/s^2}$

Conclusion

SPS KNN bars were presented in this work. Pure KNN nanopowder was used to fabricate the ceramics and compare their properties to commercial doped KNN. Thanks to electromechanical characterization good piezoelectric properties were assessed and the simulation show that interesting harvested power can be expected from a bimorph cantilever under vibration. Work is on progress to validate experimentally these results with a prototype further tested under vibration with several resistive loads.

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