New densification route of metallic supported printed multilayer for piezoelectric energy harvesting

Maria-Isabel Rua-Taborda[1,2], Catherine Elissalde[2], U-Chan Chung [2], Hélène Debéda[1]*

[1] *Université de Bordeaux, Laboratoire IMS, Talence, France;* [2] *ICMCB, CNRS, Pessac, France*

**Corresponding author: helene.debeda@ims-bordeaux.fr*

Highlights

- SPS densification of screen-printed PZT supported on a stainless substrate SS
- Multi-layer printed Au/PZT/Au/SS for energy harvesting

1. Introduction

Piezoelectric vibration energy harvesters (EH) based on $PbZrTiO_3$ (PZT) have received significant attention during these last years because of the simplicity of the piezoelectric electro-mechanical conversion and the outstanding electromechanical properties of the PZT [1]. PZT thin films (<1 µm) are often deposited onto silicon or metallic supports but are not suitable when large power is required due to their weak electromechanical coupling. PZT thick-films can bridge the 1-100 µm gap between thin films and bulk components [2]. They can be formed by the low cost screen-printing technology through a mask using mass-production methods and do not need to be assembled manually, unlike machined ceramics. It is therefore possible to create quite complex structures with a series of relatively simple fabrication steps. Printed-piezoelectric thick-films implemented on metallic substrates instead of silicon substrates already confirmed their excellent performances such as flexibility, toughness, and high-efficiency of power generation [3]. Here, the objective is to develop a printed low cost vibration piezoelectric energy harvester based on densified PZT with microstructure and electromechanical properties approaching those of commercial PZT pellets. The energy harvesting microsystem consists in a three-dimensional thick-film structure made of a thick PZT layer sandwiched between two gold electrodes deposited on a stainless steel substrate (SS). Because of the residual porosity observed in the fired PZT printed film due to the removal of the organic binder before the firing, improved densification can be obtained by adding an additional isostatic step before the firing [4,]. Also, as shown in previous work, a better compacity of the PZT thick films fired at 900°C can be observed when the PZT powder is mixed with the eutectic phase LBCu instead of the borosilicate glasses [5]. Sintering without additives is nevertheless preferred to achieve the best electromechanical properties. In this work, a co-sintering of the printed multilayer Au/PZT/Au by Spark Plasma Sintering is proposed. This original solution proposed here, would have several advantages over classical densification routes: increased compacity while reducing the firing temperature, no use of additives and no need of a pressure step before the firing. The PZT microstructure, the interfaces between the layers and the electromechanical properties required for the EH application are then investigated.

2. Methods

Screen-printing of the Au or PZT layers (Fig. 1 (b)) is performed using a DEK Horizon semi-automatic screen-printer. The substrate is previously cut at the dimensions 2 x 40 x 0,25mm^3 before the screen-printing and drying at 120°C of the Au bottom electrode, active PZT and Au top electrode layers (Fig. 1 (b)). Concerning the piezoelectric paste, two types of PZT inks are used. The first paste is made from a commercial piezoelectric PZT powder (hard PZT PZ26 from Ferroperm) blended with an organic vehicle (ESL4000from ElectroScience Laboratories). This paste is used for the SPS experiments. The second paste is made of the same PZT powder mixed with 3wt% LBCu (25wt% Li2CO3, 40wt% Bi2O3, 35%wt CuO) also blended with the ESL400 organic vehicle. This paste is for the conventional process including an isostatic pressure step (5min at 65°C and at 40MPa) before the sintering at 900°C. The gold paste is a commercial paste (ESL8836). The SPS equipment is Dr Sinter 515S. The PZT pellets are sintered in vacuum at temperature of 850°C and 875°C under an applied pressure of 50MPa. The Au/PZT/Au/SS multilayer is placed in a modified graphite set-up. The temperature is fixed at 850°C for the first attempts. Electromechanical characterization is performed using an Agilent E5063B impedencemeter.

a) b) c)

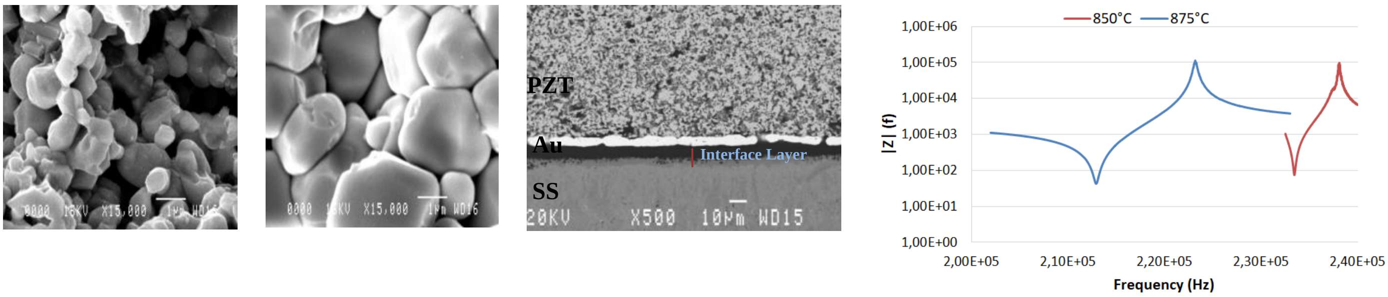
Figure 1. a) PZT ceramic fired at 875°C b) Scheme and (c) photo of the Au/PZT/Au/SS dried printed multilayer

3. Results and discussion

The microstructure of the ceramics and the printed multilayer is observed by SEM (Fig. 2), and electrical measurements allow the extraction of the free relative dielectric constant (K^T_{33}) and the electromechanical coefficient (k_{eff}). The bulk density is also calculated from the SPS sample weight and geometrical dimensions. The microstructural and electromechanical properties are summed up in table 1, they clearly show the potential of the SPS technique at 875°C compared to printed thick film and ceramics sintered conventionally at high temperature.

Table 1: Properties of SPS ceramics and printed multilayer compared with commercial PZT disk.

	Grain size (µm)	Relative density (%)	Bulk density (g/cm^3)	k_{eff}(%)	K^T_{33}
SPS ceramic 850°C// 875°C	1- 2 //2.5-4	95//97	7.3 // 7.6	25.5/30	938//1164
Printed thick film (900°C)	1-4	82	-	-	330
Conventional sintering (1200°C)	2-5	99	7.70	50	1300



a) SPS 850°C b) SPS 875°C c) Au/PZT/Au/SS 900°C d)|Z|(f) for the planar vibration mode

Figure 2. SEM images of ceramic fired at 850°C (a), and 875°C (b) with a magnification of x1500 c) SEM images of the printed multilayer d) Impedance for the PZT ceramic sintered by SPS at 850°C or 875°C

4. Perspectives

Optimization of the SPS sintering of a PZT powder from Ferroperm has been led. The temperature of 875°C appears to give the best results with properties approaching those of a PZT pellet prepared by the conventional sintering. Based on these assumptions, a PZT paste without mineral binder has been prepared and a Au/PZT/Au multilayer has been screen printed and dried on a SS substrate. This sample placed in the SPS sintering equipment is expected to give higher compacity and better electromechanical properties as the same multilayers sintered at 900°C with the help of the LBCu eutectic. Tests are under progress.

References

[1] S. Tadigadapa, K. Mateti, *Meas. Sci. Technol*. 20 092001 (30pp) (2009)
[2] C. Hindrichsen, *Sensors and Actuators A*, vol. 163, pp. 9-14 (2010).
[3] D. Zhu, S. Beeby and M. Tudor , *Sensors and Actuadors A*, vol. 169, pp. 317-325 (2011)
[4] H. Debéda, C. Lucat and F. Ménil, *Journal of European Ceramic Society*, **25**, 12, pp.2115-2119 (2005)
[5] H. Debéda, P. Clément, E. Llobet and C. Lucat, *Smart Mater*, 2015, 24, 025020, 2015

Keywords
PZT, screen-printed, multi-layer Au/PZT/Au/SS, SPS