# Lead-free KNN-based piezoceramics for ultrasonic imaging

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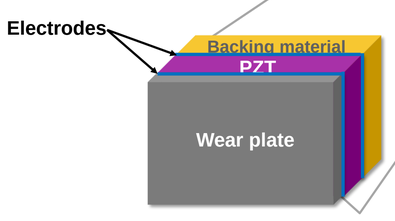
## 1 Introduction

**Ultrasound imaging system** (Fig.1) is a non-invasive medical imaging technique that has become one of the most widely used **diagnostic tools** in modern medicine for detecting prenatal anomalies and deep screening of biological tissues.

*Fig. 1.* Ultrasound imaging device.

*Fig. 2.* 3D and new generation 4D ultrasonic transducers, commonly known as medical probes

The ultrasound transducer in the probe (Fig.2) is generally made of a **piezoelectric ceramic** material such as **lead zirconate titanate (PZT)[1].**




**PZT** (Fig. 3) are the largest material group for piezoelectric devices

However, the presence of **a lead-based material** can be considered a critical issue for device working in contact with **biological tissues[2]**.

RoHS

Pb lead-free

[1]J. Holterman, P. Groen, an introduction to Piezoelectric Materials and Applications, edited by Stichting Applied Piezo, 1st edn (Apeldoorn, 2013).
[2]Directive 2012/19/EU of the European Parliament of the European Parliament and of the Council of of 4 July 2012 on waste electrical and electronic equipment (WEEE), http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32012L0019&from=EN.

## 2 Background

Among the lead-free candidates, **$K_xNa_{1-x}NbO_3$ (KNN)** has become one of the most investigated lead-free piezoelectric system

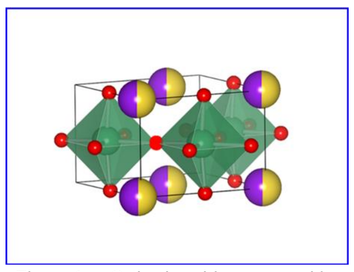


*Fig. 4.* Orthorhombic perovskite structure of the $K_{0.5}Na_{0.5}NbO_3$ phase

**KNN Properties**

- $d_{33}$ 390-490 pC/N
- $T_c$ 217-304 °C
- High chemical stability
- Biocompatibility

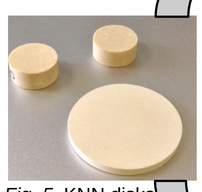
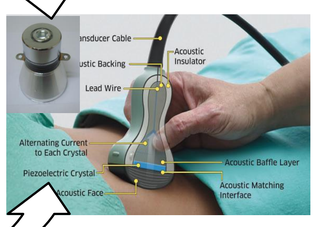


*Fig. 5.* KNN disks

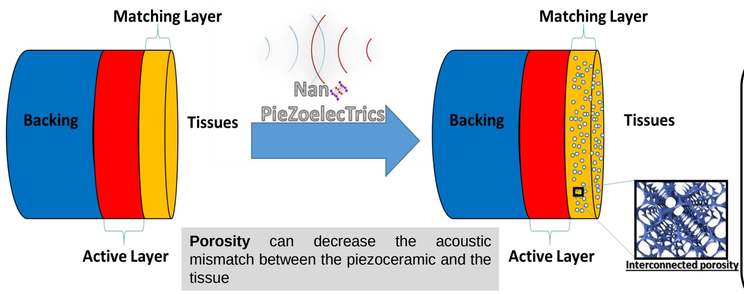
To be improved

- Frequency
- Electric properties
- Acoustic coupling
- Surface reactivity




## 3 Objectives and Methodology

**Nanopiezoeletrics** focuses on developing new piezoceramics with **interconnected porosity** in mesoporous range, characterized by promising properties specifically modulated for **biomedical application.**



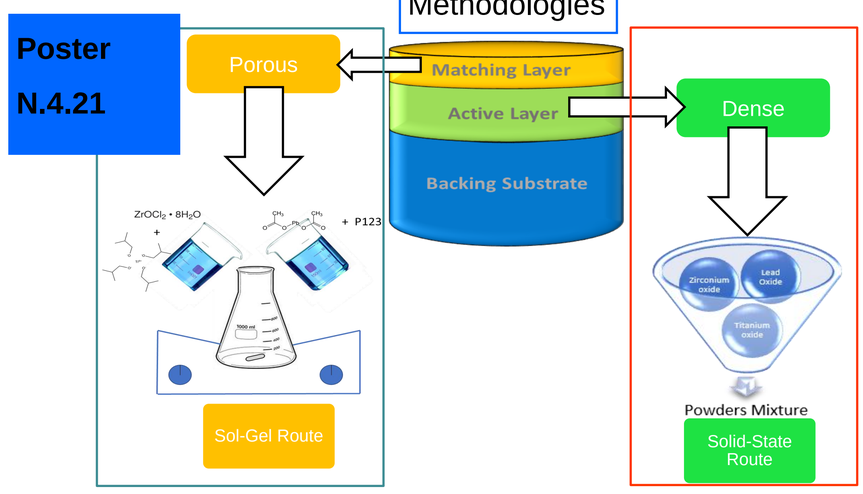

**Porosity** can decrease the acoustic mismatch between the piezoceramic and the tissue

**Objectives**

- **Development of high efficient synthetic protocol for dense and highly-ordered mesoporous Piezoceramics.**
- **Doping of the mesoporous and piezo matrices.**
- **Ultrasonic sensor prototype**

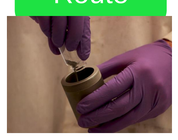
**Methodologies**

**Poster N.4.21**




## 4 Preliminary Results

**Solid-State Route**



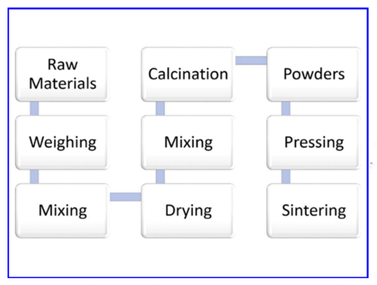
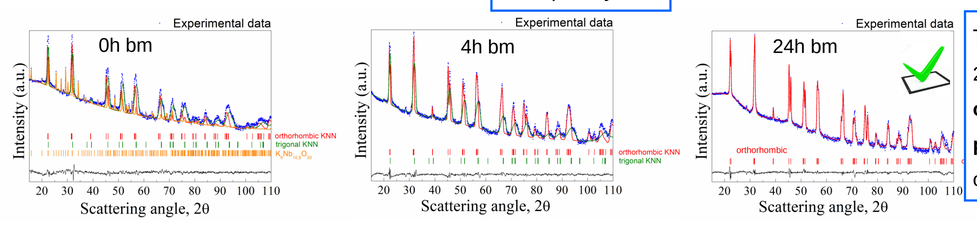



*Fig. 6.* Schematic representation of the mainly steps used in the production of KNN pellet by solid-state route.


Starting reagents: **$Nb_2O_5$, $Na_2CO_3$, $K_2CO_3$**

In this specific study the influence of the **mechanical processing (MP)** and the addition of **$MgNb_2O_6$** on the **KNN microstructure** was evaluated.

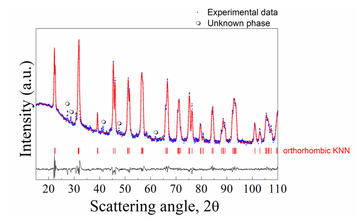
Undoped system

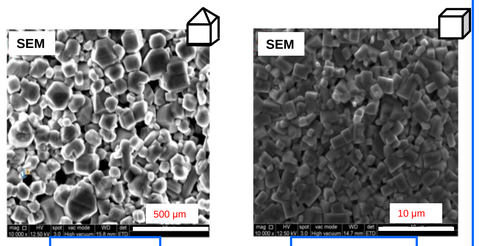



The powders milled for 24h presented a single **orthorhombic KNN phase**. A clear benefit of **MP** is evidenced.

*Fig. 7.* XRD patterns of the powders milled at different times (0, 4 and 24h) and annealed at 1000 ° C.

1wt.% $MgNb_2O_6$-doped system




After doping

Before doping

The addition of **$MgNb_2O_6$** strongly influenced the particles **dimension** and **shape**. Typical **cubic** shape of KNN particles has been **modified** with an improvement in the densification of the sintered disk.

| | Density (g/cm³) | Theoretical density (%) | Geometric density (g/cm³) |
|---|---|---|---|
| **KNN** | 3.3167 | 74 | 3.3154 |
| **KNN-1% MN** | 3.6220 | 80 | 3.5841 |

*Fig. 11.* Bulk densities of KNN-1% MN sample

## 5 Conclusions and Future plans

- Prolonged milling of the starting reagents allow to obtain pure KNN phase
- Mechanical processing decreases the calcination temperatures of the KNN samples
- $MgNb_2O_6$ addition helps to modify the cubic shape particles of KNN
- A better densification is achieved in the doped system
- Piezo-properties characterization of the as-prepared materials by PFM apparatus
- Correlation between structural and piezo properties
- Combination of the dense and porous KNN

## Acknowledgments

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