

PhD proposal

Sintering strategies for defect-controlled lead-free piezoelectric ceramics

Key words: lead free ceramics, defects, microstructure, piezoelectricity

Description:

Piezoelectric materials for transducer or actuator applications are nowadays still based on Pb(Zr,Ti)O₃ (PZT) perovskite ceramics containing toxic lead. Alternative lead-free piezoelectrics are being developed, while still not reaching the response values of PZT and imposing difficulties in the manufacturing processes, raising numerous development issues that we need to overcome. Among the potential lead-free materials, K_{0.5}Na_{0.5}NbO₃ (KNN), (Na,Bi)TiO₃/BaTiO₃ (NBT/BT) composites and (Ba,Ca)(Ti,Zr)O₃ (BCTZ) are the most promising piezoelectric compositions that we need to further improve to meet the industrial demands. Beside chemical modifications and sintering aids to produce high-quality ceramics, alternative sintering techniques are being utilized to limit species volatilization, excessive grain growth and segregation of defects, such as spark plasma sintering (SPS) and the novel cold sintering process (CSP). The progress of these techniques is crucial also from environmental stand point as they represent a means of reducing energy consumption and CO₂ emissions.

In the scope of an ongoing European project dedicated to the investigation of new lead-free piezoelectric compositions and disruptive material manufacturing technologies for sonar applications, the young researcher will investigate processes of ceramic sintering of selected lead-free piezoelectric compositions using different sintering techniques. The influence of the sintering processes on material's microstructure, defect states and functional properties will be evaluated. Emphasis will be given to the effects stemming from the size, crystallinity and surface structure of the synthesized ceramic particles (chemical environment at particles' surface, surface roughness and wettability) and interfaces in the sintered ceramics, especially grain boundaries (etching or melting, lattice reconstruction, cementation, species reduction/oxidation). Besides the objectives of the European project, the aim is also to develop environmentally friendly materials for the increasing demand of piezoelectric devices by considering the abundance of natural resources and targeting minimization of energy consumption and carbon footprint, in compliance with REACH/ ROHS regulations on hazardous substances and low consumption processes for new generations of actuators and transducers.

Objectives and methods:

Several tasks will be carried out during the PhD period towards the proposed aim:

- 1. Preparation and characterization of ceramic powders of several lead-free compositions by solid-state synthesis, mechanochemical synthesis, and powder surface modifications chosen among promising piezoelectric systems (KNN and NBT/BT or BCTZ).
- 2. Study and comparison of i) conventional sintering, ii) spark plasma sintering and iii) cold sintering techniques, available at JSI and GREMAN, and the complete characterization of the microstructures and sintering-induced defects in the ceramics, with the focus on surface and interface properties (interface structures, dislocations, and domain walls observed by SEM, TEM) and their role on the functional properties.
- **3.** Polarization and electromechanical characterization will serve as a quality check of functionalities of produced piezoelectric components. In-situ electrical conductivity measurements at different temperatures and atmospheres will help to understand the sintering-induced defect states.

Expected results:

-Student will acquire advanced knowledge on the innovative disruptive production methods to obtain lead-free piezoelectric materials and components for electronic devices, for increasing the energy efficiency of the processes.

-Student will determine and understand the relations between ceramics processing, interface chemistry and structure and functional properties of materials. Possible novel functionalities of materials produced by disruptive sintering technologies will be outlined.

Scientific supervisors:

Dr. Mojca OTONICAR from JSI (50%) mojca.otonicar@ijs.si Prof. Isabelle MONOT-LAFFEZ from GREMAN (30%): isabelle.laffez@univ-tours.fr Prof. Franck LEVASSORT from GREMAN (20%): franck.levassort@univ-tours.fr

Location:

The PhD time will be shared in two one-year periods between GREMAN laboratory in Tours, France (http://greman.univ-tours.fr/; first year) and Jozef Stefan institute in Ljubljana, Slovenia) (https://www.ijs.si; second year). The third year will be shared between the two laboratories and will depend on the ongoing research and results, and the manuscript and thesis writing.

The Doctoral diploma will be delivered at University of Tours (France) linked to GREMAN laboratory and the Doctoral School Energy Materials Earth Sciences N°552. 50 European Credits (ECSTS) will have to be collected through trainings, conferences, summer school

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Student profile: Student in Master or Engineering school in Physics, Chemistry or Materials Science. Motivated and dynamic student with strong abilities for experimental work, a good knowledge of English (written and spoken) as well as writing abilities. A research experience in a laboratory is welcome.

How to apply: The recruitment process is in 2 steps,

1) Preselection (deadline for sending is XXX 2024):

The student must fill in the forms online on (https://collegedoctoral-cvl.fr/), then click on "*before the doctorate*" and then "*topics proposed by the doctoral college*" to find out the subject; then apply with including:

- Cover letter (2 pages maximum);
- Detailed CV;
- Copy of diploma and grades: Bachelor and of Master (or equivalent for engineering schools);
- Recommendation letter from their master's internship's supervisor, indicating an initiation to research;
- Any other information helping to evaluate the application.

All applications will be reviewed, and the most promising applicants will be invited to an interview (online) with the scientific directors from JSI and GREMAN, by first presenting their background and motivation for PhD work and regarding the PhD subject, followed by a discussion.

Details of the position: PhD studentship fully funded for 3 years (European project funds), starting as soon as possible. Salary according to law (about $1800 \in$ after taxes) with the possibility to carry out complementary teaching duties.