



UNIVERSITY OF
BIRMINGHAM

16 July, 2019

School of Metallurgy and Materials
College of Engineering and Physical Sciences

Professor Tim W Button
Emeritus Professor of Functional Materials
and Devices

Ing. Bo Nan – Supervisor's Opinion on Thesis

Ing. Bo Nan graduated with BSc and MSc degrees in Powder Materials Science and Engineering from Central South University, Changsha, China in 2011 and 2014 respectively. In November 2014, he joined CEITEC, Brno University of Technology as a PhD student in the Department of Advanced Materials with the research topic concerned with an investigation of novel electroceramic structures for new sensor applications.

The work has involved three main parts, with the overall aim to demonstrate the fabrication of lead-free piezoelectric ceramics in forms and connectivities (2-2, 3-3 and 1-3) suitable for device applications, to help bridge the gap between materials science and materials engineering. Firstly, one of the promising candidates in piezoelectric lead-free ceramics, $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ (BCZT), was chosen to investigate methods for decreasing its high sintering temperature by (a) doping with lithium carbonate and (b) synthesizing the powder by a sol-gel technique. These two routes were compared with powder synthesised by conventional solid-state routes. Samples fabricated from sol-gel powder doped with 0.5 wt.% lithium carbonate and sintered at 1300°C for 2 hours exhibited credible values of $d_{33} = 447 \pm 9 \text{ pC N}^{-1}$, Curie temperature 98.7 °C and grain size $7.0 \pm 0.3 \mu\text{m}$.

Secondly, oil-based and water-based suspensions were developed for tape casting. For oil-based tape-casting, carbon and BCZT suspensions were developed with solids loadings of 25 wt.% and 65 wt.%, respectively, and used to prepare crack-free green films. The problem of hydrolysis of the BCZT powder in aqueous suspensions was solved by surface treating the powder with $\text{Al}(\text{H}_2\text{PO}_4)_3$ enabling crack-free films to be tape cast in one step. Films sintered at 1500 °C exhibited a relative dielectric constant of 1207, dielectric loss of 0.018 at 1 kHz, remanent polarization of $7.54 \mu\text{C}/\text{cm}^2$ and coercive field (E_c) of 0.23 kV/mm at 3 kV/mm.

Thirdly, Robocasting, a layer by layer direct ink writing method, was applied in shaping BCZT into 3-3 and 1-3 connectivities. An ink formulation containing a solids loading of 41.6 vol.% BCZT with processing additives (HPMC ~ 2.4 % and PEI ~ 0.03 %) was developed with the required rheology for the printing process. 3-3 samples sintered at 1500 °C exhibited the highest dielectric and piezoelectric properties, with Curie point = 86 °C, $\tan \delta = 0.021$, remanent polarization = $4.56 \mu\text{C}/\text{cm}^2$, and $d_{33} = 100 \pm 4 \text{ pC/N}$. Extremely impressive samples with 1-3 connectivity sintered at 1500 °C and infiltrated by epoxy exhibited a dielectric constant of 144 and dielectric loss of 0.035 at 1 kHz.

This work has demonstrated the shaping of lead-free piezoelectric ceramics with good properties into complex device structures and represents a significant step towards their use in applications.

During his full time PhD study, in addition to his research activities, Ing. Bo Nan participated in the GACR project "A fundamental study of the effect of synthesis and processing conditions on the structure and properties of (Ba, Ca) (Ti, Zr) O₃ lead-free piezoceramics" (Czech Republic) and IF/00951/2014 project "Microfabrication of ceramic microdevices for advanced applications - new approaches for the cost effective near-net shaping" (Portugal). He has attended an internship of 6 months in the University of Birmingham UK, and a number of internships at the University of Aveiro, Portugal, including most of his final year, where the majority of the tape casting and robocasting work was carried out. He is co-author of 4 publications (2 as first author), and has presented his work at 6 international conferences (Czech Republic, Portugal, France and

Belgium). He has also been involved in the training and supervision of bachelor students at CEITEC, and in Aveiro and Birmingham during his internships.

In conclusion, Ing. Bo Nan gained a broad knowledge of the field in the course of his doctoral studies, demonstrated the ability of independent scientific work and achieved a number of original results. I recommend that his dissertation be accepted for defense.

Yours sincerely

Professor Tim W Button