Review Report on PhD Thesis

Faculty: **Central European Institute of Technology**
Brno University of Technology in Brno

Academic year: **2018/2019**

Student: **Bo Nan**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced Materials**

Supervisor: **prof. Timothy William Button, Ph.D.**

Reviewer: **Dr. Steven Milne**

PhD thesis title: **An investigation of novel electroceramic structures for new sensor applications**

Topicality of doctoral thesis: The processing of lead-free piezoelectrics is a very topical research area given the health and environmental hazards associated with conventional piezoelectrics which contain high amounts of lead. This thesis represents cutting edge research and has resulted in publications in international journals which confirm the quality of the research: there is scope for further publications.

Problem solving and dissertation results:

A systematic and carefully carried out study aimed at developing a high-grade fabrication process for producing a lead-free piezoceramic, barium calcium zirconium zirconate (BCZT) . After investigating relevant aspects of colloid science, high quality piezoelectric thick films were produced by tape casting. The final stage of the research program addressed and overcame challenges associated with producing piezoelectric composite structures of different connectivities using a direct ink writing (additive manufacturing) technique.

A series of problems were successfully overcome, ranging from: devising the best powder synthesis method and sintering regime for fabricating single-phase BCZT powder; overcoming colloid instability and cation dissolution/hydrolysis problems during wet-processing / tape casting; devising suitable

rheological properties; overcoming a series of technical difficulties in developing direct ink writing as a new method for making 1-3 composite structures.

Importance for practice or development of the discipline: The thesis presents new methods of fabricating piezoelectric composites and new insights into various aspects of colloidal processing of an important Pb-free piezoelectric ceramic. The results will be a valuable addition to undertstanding the processing- structure-property relationships for BZZT ceramics. A notable example being its pioneering application of direct ink writing for 1-3 piezoelectric composites.

Formal adjustment of the thesis and language level:

Excellent English- no change required.

Questions and comments:

Potential Questions for the oral exam

Q1. Pages 51-52 How were lattice parameters obtained from X-ray powder diffraction data? Does the method employed warrant 4 dec places (was an internal standard employed, how mqany reflection sused in any refinement?). Also c/a ratio precision to be queried (5d ec places quotedon submitted copy) ?

Q2.Page 58 Explain why a change to sintering temperature might shift the phase transition temperatures.

q.3Page 61 Fig 4.12 The unusual profile of the 'dielectric loss' plot (O-T) in some samples (Fig b, e) should be commented upon. There seems also to be some additional low temperature anomaly in the loss plot in Fig d (~ -25 °C) below the peak temperature. Why?

Q4. During the oral exam it would be useful to discuss the rationale for selecting aluminium dihydrogen phosphate as a reagent to 'prevent hydrolysis'. Also query the

mechanism and ask if the reagent may act to reduce cation dissolution from BCZT due to it forming a surface coating on the powders.

Q5. The oral exam will provide an opportunity to discuss the reasons foir differences in zeta potential vs pH of the 4 different sample conditions (Fig 5.15). This should include comment as to the different trends in zeta potential in high alkaline electrolyte solutions (pH 11-12).

Q6. Explore the candidates understanding of the explanations presennted for the experimental trends in zeta potential vs pH (Fig 5.15).

Q.7 Probe awareness of levels of precision in pH measurements - are the very minor changes to pH over time (Table 5.1) significant? (highly unlikely)

Q.8 It is suggested that future work could try to improve functional properties by densification in the post processing procedures. What are thse methods?

END OF QUESTIONS

Optional Edits which may be implemented prior to oral exam are listed below.

Page 45. Could amend the statement stating ' no impurity phase' (this implies single phase because the XRD patterns show $CaTiO_3$ and BZT (as stated)

age 51/52 Table 1 the a and c values are given to 5 significant figures (4 dec places) but the c/a ratio calculated from these values is quoted to 6 significant figures (5 dec places) which is invalid. The values shoud be rounded to decimal places. Even 4 decimal places for lattice parameters is dubious unless an internal standard was used and an appropriate refinement methods used (that is based on multiple reflections) . The refinement method for calculating lattice parameters from XRD data should be added to Expt section (p 40).

Page 53 Fig 4.6 . The symbols used to denote extra phases should be included in the Fig caption. It would also aid clarity if the formula of the phases relating to the ICDD codes be added to the figure (top 3 patterns).

Fig 4.7 Could add a magnified scale inset plot of the high temperature > 1000 TG data to verify statement that ' a small perturbation of mass loss on the TG curve can be observed after 1200 C' . At present no mass loss anomaly at this temperature is eident.

Fig 4.10 permittivity and loss plot. There seems to be a hint of an anomaly in relative permittivity around 15-20 C, but since three plots (different sintering times) are overlaid the anomaly may be obscured. Separating the plots and using smaller symbols and finer lines may reveal something.

Page 59 para 1 The description of the d_{33}-composition plot for different temperatures is unclear and could be re-written. The statement that d_{33} remains the same when sintering time increases to 4 h only applies to the 1 and 1.5 % samples- this needs to be highlighted (there is a big jump ~ 2 fold increase in d_{33} between the 2 h and 4 h experiments for 0.5% Li. Page 59 para 2 Samples pellets (mixed oxide) are said to stick to the alumina plate (substrate) . Presumably no BCZT powder bed was employed. Zirconia plates were used for the sol-gel sample pellets. Within the section describing the properties of mixed oxide sample, a comment may be added to highlight possible effects of Al diffusion.

Page 60-61

Text and Fig 4.12 . The unusual profile of the 'dielectric loss' plot (O-T) in some samples (Fig b, e) should be commented upon. There seems also to be some additional low temperature anomaly in the loss plot in Fig d (~ -25 °C) below the peak temperature. Again at least it should be described (even if no explanation is offered).

Page 62 The sentence beginning ' From Figure 4.13(a)--- ' could be clarified.

Page 65 Maybe change 'comprehensive' to 'optimum overall'

Page 66 Explain why is a literature citation included in this table (grain size for undoped sample)?

Page 73 Could add explanation as to why shear-thinning behaviour (of C suspensions) ' can facilitate the tape-casting process' whilst Newtonian behaviour acts as a ' flowing agent' Also clarify term' flowing agent'

Page 87-. The chemical formulae of A40 Dispex should be presented (or at least generic information on this type of dispersant presented).

For a full explanation of the trends illustrated in Fig 5.15 and discussed in text page 88, a comment should be added regarding the effect of A40 Dispex on the zeta potential-pH plot (Fig 5.15).

I was not able to follow all the arguments presented in text Page 88. The second phosphate ion deprotonation is mentioned in the last sentence - over what pH does this occur? (Eq 5-3 is first one and correlated to pH 5.5-7 range).

Further comment on the possible reasons for differences in zeta potential vs pH of the 4 different sample conditions (Fig 5.15) is recommended. This should include comment as to the different trends in zeta potential in high alkaline electrolyte solutions (pH 11-12). The oral exam will provide an opportunity for these matters to be explored.

Table 5.1 and following text P 89 and 90. Drifts in pH values are common and the (in)stability in pH readings may depend on the quality and chemical history of the glass electrode. I have reservations about the reliability of differences of 0.01-0.05 pH units over a time period of 3840 mins. However the differences between untreated and treated are significant.

The author may wish to add mention of possible decreases to pH arising due to hydrolysis of dissolved metal ions/metal oxides e.g. $Ba^{2+} + 2H_2O = Ba(OH)_2 + 2H^+$.

Conclusion: A very well constructed research project, bridging materials science and materials engineering addressing challenges in processing piezoelectric composite structures of a lead-free composition, barium calcium zirconium titanate. There is clear evidence of high qualiity supervision and my reasding of the thesis indicates the candidate has conducting the experimental work with great care, shown critical thinking, achieved the objectives and produced a very good thesis.

In my opinion, the reviewed thesis fulfills all requirements posed on theses aimed for obtaining PhD degree. The thesis submitted by the candidate, Mr. Bo Nan, fully satisfies the requirements for the PhD degree, as stated in § 47 section 4 of the Law. This thesis is ready to be defended orally, in front of respective committee.

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In Leeds, date... 20th Aug 2019.....

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Dr. Steven Milne

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