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# Review Report on PhD Thesis

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

**Academic year:** 2023/2024

**Student:** Maliha Siddiqui

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

**Field of study:** Advanced materials

**Supervisor:** Doc. Ing. David Salamon, PhD.

**Reviewer:** Doc. Ing. Zoltán Lenčéš, PhD.

**PhD thesis title:** The presence of trace additives in advanced ceramics and their influence on sintering

**Topicality of doctoral thesis:**
The topic of the PhD thesis is highly actual, as there is still a growing interest to prepare hydroxyapatite-based ceramic materials with designed porosity, grain morphology and phase composition for applications in biomedicine, and the lead-free $BaTiO_3$ in the field of electroceramics.

**Meeting the goals set:**
The main objective of the work was a thorough and comprehensive analysis and better understanding the role of dopants (their type and content) on the phase composition, microstructure, in vitro bioactivity of hydroxyapatite-based ceramics and electrical properties of $BaTiO_3$-based ceramics prepared by conventional and non-conventional sintering techniques. Based on the reported results it can be concluded that the objectives of the PhD thesis have been fulfilled in the whole extent.

**Problem solving and dissertation results:**
An appropriate processing and characterisation methods have been selected to reach the goals of the thesis. The porous hydroxyapatite (HA) scaffolds were prepared by freeze-casting followed by lyophilization and sintering. Some of the samples were hydrothermally treated and characterized including their compressive strength and in-vitro bioactivity. The $BaTiO_3$ ceramics were prepared by conventional (pressureless sintering, hydrothermal synthesis) and non-conventional technique (cold sintering process). The used characterization techniques were XRD, Raman spectroscopy, SEM with EDX spectroscopy, XPS, TEM equipped with heater and electron energy loss spectroscopy (EELS). The main achievements of the work can be summarized as follows:

*Hydroxyapatite ceramics*:
- Upon the addition of $CaCO_3$ as a dopant, the phase composition is transformed from monophasic β-TCP to a biphasic calciumphosphate formulation consisting of HA and β-TCP.
- Hydrothermal treatment of the sintered $CaCO_3$ doped HA scaffolds showed a significant change in microstructure, varying from whisker-like, needle-like to hexagonal rod-like morphology and exhibited better bioactivity.
- $Ca^{2+}$ ion plays a crucial role in the increase of HA/β-TCP phase ratio.
- After freeze-casting the HA scaffolds exhibit a reasonable compressive strength of around 6 MPa.

*Barium titanate ceramics*:
- Sr-doped $BaTiO_3$ prepared by cold sintering at 225 °C contained also secondary phases, which indicates the incomplete incorporation of $Sr^{2+}$ dopant into $BaTiO_3$ crystals.
- Cold sintering process induced the tetragonal to cubic phase transition.
- Post-annealing of cold sintered $BaTiO_3$ at 500 °C is the optimum annealing temperature.
- TEM and XPS analysis showed the segregation of $Sr^{2+}$ on the surface of $BaTiO_3$.
- The room temperature dielectrical properties of the doped $BaTiO_3$ are influenced by the dopant ($Ba^{2+}$ or $Sr^{2+}$).

**Importance for practice or development of the discipline:**

There is a great potential to apply the results of the thesis in the practice, either the HA-based bioceramics in the medicine as bone replacements, or Sr-doped $BaTiO_3$ ceramics as transducers or capacitors for energy storage. There is also given a deeper insight to the processes taking place during the cold sintering process. However, further investigation is required in this field.

**Formal adjustment of the thesis and language level:**

The thesis is well structured. The introduction to the thesis provides an effective overview on the topic with reference to appropriate recent literature. The literature review is good (206 references) and gives a relevant information about the studied materials (HA, $BaTiO_3$), their processing and used characterisation methods. It is worth mentioning that most of the references are from the last 15 years, showing a topical issues. The experimental part is well described, the results are clearly reported and well documented. The figures, schemes, and tables are shown properly as well. Relevant methods have been chosen for the characterisation of the materials.
The English is good in the Introduction, but it should be improved in the Results and Discussion. Sometimes it was difficult to understand the content of the sentences.

**Questions and comments:**

I have the following ***comments***:

1) Variables should be written in italics format (e.g. on page 40 after Eq. 13, etc.).
2) Page 54: Figs. 26a,b,c are XRD patterns, while the Raman spectra are in Fig. 26d.
3) Page 58, Table 12: Do not use ± symbol for the interval (not 88.35 ± 89.85, but 88.35 – 89.85).
4) Page 62: It is better to write the vacancies $V$ in italics format in the formula of oxyhydroxyapatite, to avoid the mixing with vanadium.
5) Page 68, Fig. 39a: The title of X axis should be Temperature, on Y axis the units of volume should be $Å^3$.
6) Page 73, Fig. 43f: The list of elements should be in larger font size, because it is very difficult to read it even at higher magnification.

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***Questions***:

1) Page 37, Fig. 16: During the cold sintering process using the SPS furnace the die was made of graphite, while the punches were made of WC. Was there any temperature gradient due to the different materials used for pressing and sintering?
2) Page 39, 4.2.3. Post annealing of samples: It is written „After each round of treatment, the samples were characterized before going to the next post-annealing temperature." Does it means that e.g. sample CS11 was annealed at 500°C/3 h + 800°C/3 h + 1100°C/3 h?
3) Page 40, line 4: „To reduce the carbon contamination the CS2 was crushed and heated for 3h in vacuum." What was the temperature of annealing? Did you try to evaporate the remains of acetic acid? Was there any other source of carbon?
4) Page 49, Table 6: How many grains were evaluated to determine the aspect ratio of HS4 and HS5 grains? Were there about 100 grains? When I have analysed the well visible whole grains (about 10), the aspect ratio was higher: 5.15 instead of 1.54 for HS4 and 2.35 instead of 1.70 for HS5.
5) Page 51, Table 8: Why is the mass gain of samples FS-0 and FS-2 different, if the mass before and after immersion to HBSS simulated solution is the same? Is it a misprint in Table 8?
6) Page 53: „...drastic variation of $\varepsilon_r$, it was much worse for doped material." But both materials were doped (either with $Ba(OH)_2 \cdot 8H_2O$, or $Sr(OH)_2 \cdot 8H_2O$). Do you mean Sr-doped materials?
7) Page 56: „The survey spectra of CB2 sample confirmed the presence of Ba, Sr, Ti, and O." What was the source of Sr in CB2 sample?
8) Page 58: „However, this phase delayed in PLS sample till 1100 °C (Fig. 30 c, and d)." What do you mean by delayed? Do you mean remained?
9) What is the reason that $\varepsilon_r$(CS11) < $\varepsilon_r$(CB11) in Fig. 34? Higher porosity of CS11 sample (Fig. 33)?
10) Page 70: „ ... the apparent peak splitting approximately at 44° associated to (002) plane" The XRD pattern starts from 44.5° in Fig. 40, so the reader cannot see the pattern at 44°. Most probably you mean the diffraction peak at ~44.8°.
11) Page 72: „After heating up the CS2 sample in the TEM microheater to 1200 °C the dopant moved from the edges toward the core." However, it seems to me from the Sr map in Fig. 42 that Sr diffuses to the neck, or edge of the necks (area with high curvature). Can you comment your observation in more details?

**Conclusion:**

The dissertation represents a good scientific level and great deal of work. All experiments were well arranged and the measurements techniques and methods were correctly applied. The results are well presented, although, as always in the cutting-edge research, the interpretation and discussion can be extended and more in-depth.

A valuable results have been achieved for the preparation of hydroxyapatite-based scaffolds for biomedical applications and for $BaTiO_3$ ceramics for electrotechnics applications.

It can be concluded that the thesis has a good quality and fully complies with all the conditions and requirements for earning the PhD degree in the field of advanced materials.

In my opinion, the reviewed thesis fulfills all the requirements posed on theses aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.

In Bratislava, 30.8.2024

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Doc. Ing. Zoltán Lenčéš, PhD.