Referee's report on Doctoral Thesis by Elizabeth Vakkechalil John (married Simon)

"Spectroscopic investigation of lattice dynamics in multidomain ferroelectrics"

The proposed thesis focuses on study of ferroelectric domains in thin epitaxial films and ceramics of some ferroelectric perovskites. The main used method is far infrared reflection spectroscopy (both unpolarized and polarized) supplemented with Raman spectroscopy and piezoresponse force microscopy. Foundation for interpretation of reflectivity spectra of samples with a domain structure is Effective Medium Approximation. Bruggeman formula, Lichtenecker formula and model by Arlt and Peusens were tested.

The thesis is divided into 8 chapters including Introduction and Conclusions. A brief proposal to future investigation of unresolved issues is added as chapter 9. Basic information on ferroelectrics is summarized in chapter 2. Experimental techniques including methods of evaluations of experimental results are described in chapter 3. Chapter 4 deals with lead titanate ceramics, chapter 5 with lead titanate epitaxial films. More detail treatise on lead titanate films deposited on lanthanum aluminate substrates can be found in chapter 6. Piezoceramics lead zirconate titanate is studied in chapter 7; especially effect of electrical poling and depoling is investigated in details. The thesis cites 179 references.

The text is well-structured with only a small number of typing errors. The author logically transfers from the description of experimental results to discussion and explanation. The figures are clear and well illustrate the subject matter. It is demonstrated that the used techniques are very useful for domain structure investigation. The novel information on domain structure of several types of samples was obtained. The results were published in 7 papers in reputable international journals (Journal of Applied Physics 2x, Physical Review, Ferroelectrics, Phase Transition 2x, Chemistry of Materials) and 2 papers are in progress. The candidate is the first author in three papers.

Only marginal inaccuracies can be found in the text: e.g. inconsistent use of symbols n^*, $\tilde{n}$ and n for complex refractive index in part 3.2.3.4 (page 37, 38), α instead of α_1 in formula (3.16). The words "polarization, polarized, depolarized" have to be used carefully, e.g. page 108: "*As the specimen was heated above the phase transition temperature, the cooling spectra will be depolarized*" It was depolarized incident infrared radiation (experimental set up polarizer – sample – analyzer) or electrical polarization of the sample was modified by heating above phase transition? I believe that the latter choice is true.

The source / sources of the samples should be given explicitly. I guess that at least majority of epitaxial films comes from Nancy University (France).

The candidate worked in an experienced team engaging successfully in physics of ferroelectrics for a long time, including far infrared measurements. Commercial equipments were used. Therefore, a question comes out what new techniques or improvements of recent methods (including modeling) were done personally by Mrs. Simon.

Questions

1. What properties of thin films are desirable for future application, like nonvolatile memories, sensors, or actuators? What is the most promising combination of substrate and film?

2. Some extraordinary spectral bands have been revealed in PTO ceramics and they have been assigned to geometric resonances. Can you briefly and illustratively outline their cause?

3. Effective medium theories are often used taking into account voids in porous materials. Do you think that porosity of $PbTiO_3$ ceramics could considerably influence its reflectance spectra and induce geometric resonances?

The thesis presents a large number of original results focusing on domain structure of ferroelectric ceramics and epitaxial films. Mrs. Simon proved ability to scientific work and I recommend that the thesis is accepted for the defence.

Praha, 3.5. 2012

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