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To
Prof. Zdenek Nemecek

Report on the PhD manuscript entitle
"*Spectroscopic investigation of lattice dynamics in multidomain ferroelectrics*"
by Elizabeth Vakkechalil John (married Elizabeth Simon).

The work performed by Ms. E. Simon aims to understand the origin of the infrared (IR) response of multidomain lead-based ferroelectric oxides in order to get insights into to the domain structure of these materials. The infrared results are confronted to direct structural observations obtained by piezoelectric force microscopy (PFM). Special attention is brought to lead titanate $PbTiO_3$ thin films deposited on substracts inducing either tensile or compression stress into the films.
These studies are preceded by a theoretical description of the infrared response of a $PbTiO_3$ ceramic. Among the different models proposed to predict the experimental effective permittivity, only that based on a domain structure similar to the case of tetragonal $BaTiO_3$ ceramics reproduces the geometrical resonances observed experimentally. The latter superpose in the IR-spectra to the polar modes expected in $PbTiO_3$ single crystal. These results reveal that geometrical resonances observed in IR absorption can bring valuable information about the domain structure in the grains.
In thin films, the frequency of the modes is shifted upward or downward depending on the misfit strain. Moreover geometrical resonances and lifting of the selection rules between E- and A_1-symmetry vibrations, constitute a signature of a domain state that could be partially described directly from the IR-absorption spectra. The results are complemented by PFM images, and lead to a more quantitative description of the complex local structure of the films. Thickness and temperature dependence of the domain structure is also investigated and discussed.
The last experimental section of the manuscript describes a vibrational study of poled PZT samples. It reveals an anisotropy of the polar phonons when the incident field is polarized parallel or perpendicular to the poling direction. This translates into frequency shifts of the IR-bands revealing the ability of the techniques to probe poled and unpoled processes.

From a theoretical point of view, the effective medium approach developed by Ms. E. Simon in her thesis provides new and valuable information for the description of the rather complex IR-response of multidomain ferroelectric materials. The relation between resonance modes and the domain structure constitutes for me an important contribution of the thesis. Overall, the progress in the description of the reflectivity spectra of structured materials, combined with the very simple operating mode of the Fourier-transform IR-spectroscopy motivates further fundamental research, and promotes the technique for industrial concerns, such as structural characterizations. This holds particularly for ferroelectric thin films and poled PZT samples, due to their very broad industrial application range.

Finally, the manuscript is well organized, clear, and well written. The results have been disseminated in seven articles submitted in scientific journals, showing the interest of the findings for the scientific community and therefore the author ability for creative scientific work.

During the thesis defense, I would like to hear a brief response to the additional questions below :

1. According to Fig. 5.1 one can expect that $PbTiO_3$ thin films on certain cubic substrates may undergo a transformation between distinct structure arrangements. How should such transformations manifest in the IR spectra ? Was it ever observed ?

2. This thesis reports about signatures of domains in spectroscopic studies of thin films and ceramics. I wonder whether similar effects have been observed in single crystals.

3. I would like to know the specificities, the advantages and the disadvantages of IR-absorption spectroscopy as compared to Raman spectroscopy for the study of the vibrations in thin films and ceramics ?

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