Reviewer's Report on Doctoral Dissertation for PhD Degree

Candidate: MSc André Maia

Title of Theis: Static and Dynamic Magnetoelectric Coupling in Multiferroics

Dissertation Supervisor: RNDr. Stanislav Kamba, CSc., DSc.

Institution: Institute of Physics of the Czech Academy of Sciences

The presented thesis is devoted to the experimental research of ceramic materials that show the coexistence of mutually influencing antiferromagnetism and ferroelectricity. They belong to multiferroics, materials with promising potential for applications in spintronic, data storage, and electrically tunable microwave devices. Experimental studies of specific phenomena in three types of materials that exhibit both ferroelectricity and antiferromagnetism are presented. The role of magnetoelectric coupling and soft mode in the emergence of multiferroicity is emphasized.

The candidate and co-authors published the main results of these studies in four articles in recognized peer-reviewed journals (Journal of the European Ceramic Society, 2 PRB, PRM). Copies of the papers can be found as attachments to the thesis.

In the introductory chapter of the thesis, basic physical concepts and underlying mechanisms responsible for ferroelectric and multiferroic phenomena are introduced comprehensively. Unfortunately, adequate information on the magnetic aspects of the multiferroic story has been almost omitted. Only a few limited notes associated with some specific cases can be found. The candidate may like to include some relevant notes in his defense presentation.

Comprehensive information on experimental techniques that the candidate himself used for experiments (Fourier transform infrared, THz time-domain and Raman spectroscopies, pyroelectric current measurements) is given in the second chapter. For other methods used during the study by collaborators, the candidate refers only to the information provided in the attached publications. One would prefer here global information on the methodology and strategy of presented studies. This would demonstrate the ability of the candidate to be a true experimenter. The candidate may like to include some relevant notes in his defense presentation.

The core of the thesis, i.e. the main results with the corresponding discussion, which have been published in the papers mentioned above, are presented in the last 3 chapters and the Conclusion. The candidate listed his contributions to the related publication at the end of each subsequent chapter. This information documents that his participation in each study was decisive for its success.

The paper **Can the ferroelectric soft mode trigger an antiferromagnetic phase transition?** demonstrates the multiferroic aspects of the behavior of the ferroelectric antiferromagnet $BiMn_3CrO_{12}$ in which a ferroelectric transition (FET) and antiferromagnetic phase transition (AMFT) are observed at (almost) the same temperature. The authors were the first to claim that the displacive FET at 125 K triggers an AFMT that appears at the same temperature. With further cooling $BiMn_3CrO_{12}$ undergoes an AFM1 to AFM2 transition accompanied by a considerable increase in ferroelectric polarization. Here they reject the existence of the second ferroelectric transition proposed in previous publications and interpret the phenomenon as a change in magnetoelectric coupling.

In the paper **Two displacive ferroelectric phase transitions in multiferroic $BiMn_7O_{12}$** a material exhibiting several structural phase transitions between low-symmetry crystallographic phases was studied. Results of the thorough investigation by the microwave, terahertz, infrared, and Raman spectroscopies enabled them to ascribe two structural transitions above room temperature to displacive

ferroelectric transitions. The weak dielectric anomalies observed at low-temperature magnetic phase transitions were attributed to the effect of strong magnetoelectric coupling in $BiMn_7O_{12}$.

The last two papers **Magnetoelectric properties of $TbMn_{1-x}Fe_xO_3$** and **Modifying the dynamic magnetoelectric coupling in $TbMnO_3$ by low-level Fe^{3+} substitution** are focused on the effects of substitutions of the Fe^{3+} ions for the Mn^{3+} ions on the balance of static and dynamic magnetoelectric coupling between the cycloidal modulated antiferromagnetic phase and the ferroelectric phase. It is argued that the substitution-induced evolution of low-lying electromagnon excitations activated by dynamic magnetoelectric coupling indicates different mechanisms for static and dynamic magnetoelectric coupling.

I have a few questions for the candidate.

What is the relationship between magnetoelectric, magnetoelastic, and electroelastic coupling?

What microscopic mechanism causes the soft mode? What triggers the antiferromagnetic phase transition in $BiMn_3CrO_{12}$ at 125 K?

The application of a magnetic field usually leads to a decrease of T_N. What can happen with the ferroelectric transition in $BiMn_3CrO_{12}$ in a magnetic field?

The considerable increase of ferroelectric polarization at the low-temperature magnetic phase transition in $BiMn_3CrO_{12}$ is interpreted as the signature of enhanced static magnetoelectric coupling. In Chapter 3, I did not find a single mention of the crystal structure. Would it not be appropriate to know the details of the crystal structure at temperatures above and below the discussed phase transitions for interpreting the observed phenomena and why?

Antiferromagnetic ordering can be suppressed by a metamagnetic transition to a paramagnetic phase induced by a high magnetic field. In Ising antiferromagnets at temperatures well below T_N, the first-order metamagnetic transition to polarized paramagnetic phase (field-forced collinear alignment of magnetic moments resembling a collinear ferromagnet) is sometimes observed. What effects on the ferroelectric phase in a multiferroic with a strong magnetoelectric can be expected at the metamagnetic transition in each case? Can any example be found in the literature?

In conclusion, I would like to note that the candidate in his thesis presents the original results of well-focused studies of various effects of magnetoelectric coupling in several multiferroics. These studies were published in four articles in recognized peer-reviewed journals, underscoring the quality of the research. The thesis is written in good British English, with occasional minor grammatical errors and typos.

MSc André Maia has undoubtedly demonstrated his capability of performing independent research and producing valuable results. I believe that this thesis meets all the requirements for a Ph.D. dissertation and recommend that the applicant be awarded a doctoral degree after a successful defense.

In Praha 15 September 2024 Prof. RNDr. Vladimír Sechovský, DrSc