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Reviewer's report on doctoral thesis

Static and dynamic magnetoelectric coupling in multiferroics

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The thesis of Andre Maia under supervision of S. Kamba, DSc. deals with search and investigation of magnetoelectric coupling in several dielectric materials to prove their multiferroic character. The work is based on four scientific papers published in 2023-2024. The theme of the thesis is topical as magnetoelectric coupling and multiferroic behaviour is currently a hot topic in solid state physics. It is not only due to its rich physics but also because of future potential applications in non-volatile electronic memories, magnetoelectric sensors, etc.

The thesis, based on published papers consists of six chapters, classically the Introduction, Experimental part and untypically Results divided to three equal parts according to the materials studied and Conclusion (not numbered). The text is relatively brief fitting to 40 pages. Second part of the thesis consists of the preprint of four papers included in the thesis. The papers were published in respected impacted journals.

The first chapter lists the papers written by the applicant (he is a first author in all these papers, with many authors from various institutions) and summarizes their content. The following subchapters introduces the physical fundaments of ferroelectric materials, the existence of multiferroicity understanding here as simultaneous existence of magnetic and electric ordering and their static and dynamical coupling. Unfortunately, the chapter is written in very dense mode on the expense of more detailed explanation. Thus, non-expert in the field (as me) has very hard time to understand it. The chapter ends with describing the electromagnons and directional dichroism and it somehow ends suddenly. I am missing some summary what is going to be investigated, how it is related and what is the scientific question to be solved.

Following four pages are occupied by description of experimental set-up describing infrared, time domain terraherz, and Raman spectroscopies and the measurement of pyroelectric current, the methods what was used by author in characterization investigated materials. But again, the text is too dense with no figures provided which can facilitate the understanding.

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The results are listed in three chapters summarized four papers forming the thesis. The first deals with the complex perovskite $BiMn_3Cr_4O_{12}$, second with simpler "pure" $BiMn_7O_{12}$, and the last chapter with iron-doped $TbMnFeO_3$ materials published in two papers. Each chapter brings some text and selected figures copied directly from the published papers. This is a pity; the more detailed description would be better and the caption of figures could be extended to facilitate understanding. Each of the result chapters consists of a final note about author's contributions (mostly spectroscopy measurement) and statement that he wrote the paper, even though the corresponding author is often somebody else from extensive list of the authors (mostly supervisor).

The conclusion well summarizes the work done, only I would suggest omitting the first self-flattering sentence, anyway the same is written again in the end.

I would also like to point out that figure captions are often too concise and brief and due to that the figure cannot be understand on its own. Captions are too literary taken from the papers and do not bring any broader context which is a pity.

In general, about text; it is mostly well written without many misprints. The sentences are, however, sometimes convoluted and it is hard to understand that the author want to say. There are several mistakes due to inattention. The list of papers after Conclusion is somehow mixed and do not correspond the labels. Also, on page 28 the text is referring to fig. 10a and b but only 10b figure is shown. On the contrary, Fig 17 has three parts, but caption is referring only to two of them.

Considering Bi based materials, one would expect from the logic that the description will start with $BiMn_7O_{12}$ and then proceed to more complex material with Cr. Here it is just opposite. Moreover, one would expect some comparison, but it is hard to come by. The first chapter is titled by a question and based on the title my question is: Is it fully clear that ferroelectric soft mode trigger antiferromagnetic order and what is the most important evidence? Cannot this be just opposite way, i.e. antiferromagnetism induces the ferroelectricity? Why there is no magnetic measurement shown?

Second part demonstrates the existence of two displacive ferroelectric transitions in $BiMn_7O_{12}$ at high temperatures connected with structural changes and several low temperature magnetic transitions to antiferromagnetic state of individual sites, i.e. ordering of B sites, then A sites and new order of A and B. In this context, I wonder what is the connection between ferroelectricity at high temperature and low temperature AFM transitions? Does AFM transition modify the ferroelectric behaviour and how?

Third part deals with the effect of 2 and 4%Fe doping to $TbMnO_3$ substituting Mn. It is shown that even that small doping strongly alternates the properties of the ferroelectric materials demonstrating the sensitivity of ferroelectric material. Here I am wondering if the effect cannot

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be ascribed to itinerant character of Fe magnetic moment in comparison with localized moment on Mn. Can you say something about that? Does the Fe doping modify the structure? I also wonder why in this chapter is the magnetic field marked as B not H as in previous one? I see, it is published this way, but I would keep SI units and marking. The letter B usually marks magnetic induction, so, what is the difference between magnetic induction and magnetic field? For me it is also difficult to talk about frequency in inverse cm not in Hz. And one more question do you have any explanation why 4 T (which is not low field, as stated) is a boundary for different behaviour? Or is the number just an accident?

Despite the mild criticism I believe that presented work demonstrates the ability of the author to independent work and creative thinking. As all results presented in the thesis were already published and thus evaluated by scientific community to be worth of publishing and dealt with, my role can be only minor, and I reckon that the written text satisfies the requirement for PhD thesis.

I recommend the presented thesis to be accepted for consideration to award the PhD degree.

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