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Review of the thesis
"Magnetoelectric properties of ferromagnets/ferroelectrics layered heterostructures"
by
mgr. Andrei Sazanovich

The thesis has been prepared in the Polish Academy of Sciences in Warsaw, its supervisor was Professor Henryk Szymczak. The Practical Materials Research Centre of Belarussian Academy of Sciences, and International Laboratory of High Magnetic Fields and Low Temperatures in Wroclaw were the cooperating institutions.

The main results of this thesis have been published in four papers in the international journals registered in the Web of Science database and in the list of journals accepted by Polish Ministry of Science and Higher Education:

1. A. Sazanovich, Yu. Nikolaenko, W. Paszkowicz, V. Mikhaylov, K. Dyakonov, Yu. Medvedev, V. Nizhankovskii, V. Dyakonov, H. Szymczak
   Magnetic and ferroelectric ordering in the $TbMnO_3$ film
   Acta Physica Polonica A, 125(1):128, 2014
2. A. I. Stognij, N. N. Novitskii, S. A. Sharko, A. V. Bespalov, O. L. Golikova, A. Sazanovich, V. Dyakonov, H. Szymczak, V. A. Ketsko
   Effect of Interfaces on the Magnetoelectric Properties of heterostructures Co/PZT/Co
   Inorg. Mater., 50(3):275, 2014
3. A. I. Stognij, N. N. Novitskii, S. A. Sharko, A. V. Bespalov, O. L. Golikova, A. Sazanovich, V. Dyakonov, H. Szymczak, M. N. Smirnova, V. A. Ketsko
   Effect of Cobalt Layer Thickness on the Magnetoelectric Properties of $Co/PbZr_{0.45}Ti_{0.55}O_3/Co$ Heterostructures, *Inorg. Mater.*, 49(10):1011, 2013
4. A. Stognij, N. Novitskii, A. Sazanovich, N. Poddubnaya, S. Sharko, V. Mikhailov, V. Nizhankovski, V. Dyakonov, H. Szymczak
   Ion-beam sputtering deposition and magnetoelectric properties of layered heterostructures $(FM/PZT/FM)_n$, (where Co or $Ni_{78}Fe_{22}$ is in place of the FM).
   Eur. Phys. J. Appl. Phys., 63:21301, 2013.

The doctoral thesis has been prepared according to the "new rule" of The Polish Law on Higher Education, which allows a thesis to be presented as a set of published papers followed by additional extended comments. The thesis consists thus of such comments completed in five chapters named the *Introduction, Aims, Experimental, Results, and Conclusions,* and of four papers attached *in extenso* to the thesis. All of the chapters are written very interestingly, with no redundant information, and are well elaborated. Perhaps, when describing different type of materials which reveal magnetoelectric properties, a distinct stress should be put on the type of heterostructures investigated in the thesis.

On page 15 the author wrote that the essential objectives of the thesis were:

1. *Analysis of methods and techniques of preparation, and investigation of the new film structures with desired magnetoelectric properties.*
2. *Examination of size effect on the magnetoelectric properties of the ferromagnetic/ferroelectric heterostructures, where the mechanism of strain mediated coupling exists. To achieve this goal the*

ferromagnetic films of metalic Ni and Co, alloy NiFe or TbMnO3 manganite were grown on ferroelectric PbZr1-xTixO3 (PZT) or SrTiO3 substrates, respectively;

3. *Investigation of the influence of quality and stability of ferromagnetic/ferroelectric interface on the magnetoelectric properties of the heterostructures.*
4. *Study of the influence of number, configuration and chemical composition of ferromagnetic and ferroelectric layers in the new layered heterostructures on the value of ME effect.*
5. *Study of the influence of resonance properties on the magnitude of magnetoelectric effect.*

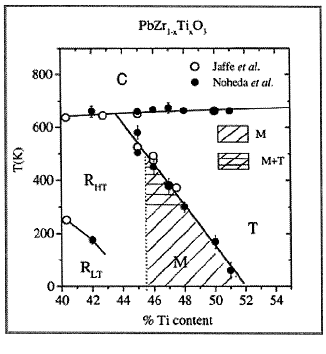
I comment on them successively below:

Re. 1

The techniques of preparation have been elaborated very clearly. The process of surface smoothing, ion-beam sputtering system and magnetoelectrical measurements with a photo of experimental setup have been well described and presented.;especially the description of details of how and at which conditions the magnetoelectric properties were detected brings no doubts that author had sufficient skills to carry out experimental works. The important thing was that the author made tests to find out whether substrates can produce a magnetoelectric signal. The fact that substrates do not contribute to the overall magnetoelectric response certainly allows making proper conclusions.

Re. 2

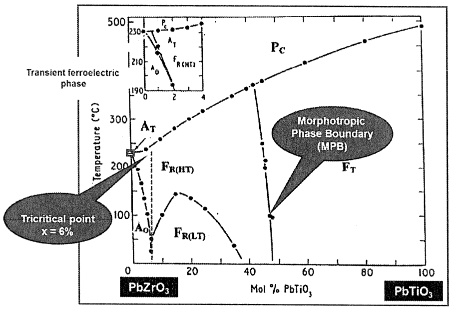
This goal seems to have been obtained. I use the word "seems" because I am not convinced that the size effect and strain mediated coupling were examined broadly enough. While the procedure of growing the thin films on PZT substrate cannot be questioned, my objections are connected with poling process of the heterostructures obtained. Namely, the $PbZr_{0.45}Ti_{0.55}O_3$ composition used belongs to compositions lying near the so called morphotropic phase boundary. It means that the piezoelectric properties are of the highest value among the PZT compounds and even between all known ferroelectrics (they are more than 1000 times larger than in quartz). To get it, a special poling procedure has to be kept. The most efficient is that conducted at a temperature not higher than 200°C (the author made poling at 150°C) and electric field strengths not exceeding 1-2 kV/mm (the author made poling in a high field, of the 4kV/mm strength). At high electric field strengths the electric conductivity of PZTs is quite high and may destroy the state of ceramic effective polarisation achieved. It would mean that the relaxation of stresses in heterostructures could be different for different thicknesses of the ferromagnetic layer (because the higher state of polarisation the higher the change of PZT sizes). Similar comments as for the poling process are valid for another PZT compound used, i.e. $PbZr_{0.2}Ti_{0.8}O_3$.

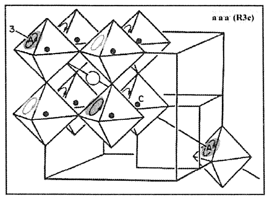


It has to be mentioned that the PZTs used were chosen so as to avoid the coexistence of phases of different symmetries, as it happens at $PbZr_xTi_{1-x}O_3$ compounds for 0.46<x<0.52, in which the coexistence of rhombohedral R_{HT}, monoclinic M and tetragonal T phases takes place (Noheda et al, Phys. Rev. B, 63, 014103, 2000).

However, the composition of $PbZr_{0.45}Ti_{0.55}O_3$ is very close to the region in which the phase diagram is really complex (see Figure on the left). Having in mind that there are compositional fluctuations in ceramics, $PbZr_{0.45}Ti_{0.55}O_3$ seems to be a substrate that does not give a homogenous strain. I have to say that I did not find a comment in the thesis on how the calculations presented in Table 4 have been done (and who did them).

For the $PbZr_{0.2}Ti_{0.8}O_3$ ceramics there is no a problem with phase coexistence, but below ca. 120°C the structure of this ceramics possesses the rhombohedral symmetry with quite complex oxygen tilts. I mention this also from the point of view of strain relaxation in heterostructures. Phase diagram of PZT and a pattern of octahedral tilts in the R3c phase is shown below.





Re. 3
This goal has been achieved indeed. The author claims that the value of magnetoelectric voltage coefficient was achieved for heterostructure built on $PbZr_{0.2}Ti_{0.8}O_3$ ceramic and permalloy. The room temperature magnetoelectric voltage coefficient equals to 250 mV/(cm Oe) at the frequency of 100Hz in magnetic field of 0.05 T was observed for triple-layered Py/PZT/Py heterostructre with thicknesses of 80, 20 and 80μm respectively, and 2μm of ferromagnetic interlayer.

Re. 4
In fact the text of Re.3 contains a comment on the goal 4 as well.

Re. 5
The author has provided the following conclusion: *"It should be noted that magnetoelectric effect essentially depends upon frequency of alternating magnetic field and has a resonant behaviour at low frequencies. Its maximum value is observed in the region of 50 -150 Hz".* No further details or comments have been given: I mean an answer to the question why the frequency range is so low. The range of piezoelectric resonances for sizes of heterostructures used, as that in Figure 3.3 on page 17, should not be found in such low frequencies. Piezoelectric resonances would be expected to have the order of at least at hundreds kHz. A comment or a discussion on these low frequencies would be thus desired.

The thesis is well written and can even be read by scientists from other fields. However, one can find language and grammar errors in the text. While the origin of these kind of errors might be simply an oversight, two of them have to be mentioned from the professional point of view:

1. On page 7 it is written: "*Relations between electric and magnetic parameters are obtained by differentiation the free energy with respect to E and* ***M****:".*
   The correct version is the following: "*Relations between electric and magnetic parameters are obtained by differentiation the free energy with respect to E and* ***H****:"*
2. On page 22 it is written: "*Investigation of magnetic and magnetoelectric properties of multiferroic $TbMnO_3$* film grown onto the **ferroelectric $SrTiO_3$** ...".
   A correct version is the following: "*Investigation of magnetic and magnetoelectric properties of multiferroic $TbMnO_3$* film grown onto the **ferroelastic (antiferrodistortive) $SrTiO_3$** ... ".

As far as I am able to estimate it, the references are those needed and properly cited in the text. However, I am a bit surprised that the paper "Revival of the magnetoelectric effect" by M. Fiebig published in the Journal of Physics D - Applied Physics 38, No. 8, p. R123-R152 (2005) has not been included in the references. At least from the point of view of values of the magnetoelectric effect, which can be of the order of few V/Oe·cm (Fig.15 ibid), while the value reported in the thesis - and called high value - did not exceed 250μV.

I would also expect that the author of the thesis would indicate his share in the papers published. This remark seems justified because only in one of these papers mgr Sazanovich is the main author. This is a paper that concerns $TbMnO_3$, but most of the papers included in the thesis deal with heterostructures on PZT substrates.

Irrespective of the high value of thesis and conclusions based on it I would like to know the opinion of the author about possible applications of heterostructures investigated in the framework of his thesis. I am interested in an answer because very often one can still find a statement similar to the following: *"At present these phenomena are primarily interesting from the point of view of basic research rather than applications".*

At the end of this review I declare that, in spite of the criticism made above, the thesis fulfils the conditions required by Polish law and a public defence can take a place.

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