REVIEW

by competition for the academic position "Professor"
Professional direction: 4.1. Physical sciences
Scientific specialty " Electrical , magnetic and optical properties of the condensed matter "
(multiferroic properties on bulk samples and nanomaterials)'
according to the announcement in the State Gazette, no. 102/08.12.2023
for the needs of Forestry University,
with candidate Assoc. Prof. Dr. Iliana Naumova Apostolova

Reviewer: Marin Mirchev Gospodinov, Professor, DSc, ISSP-BAS

Assoc. Prof. Dr. Iliana Naumova Apostolova is the only candidate in the competition for the academic position "Professor", announced in the State Gazette, issue 102 of 08.12.2023. in Professional direction : 4.1. Physical Sciences, Scientific specialty " Electrical , magnetic and optical properties of the condensed matter (multiferroic properties on bulk samples and nanomaterials) for the needs of Department of "Mathematics, Physics and Informatics" at Forestry University - city of Sofia.

1. **General characteristics of the presented materials.**

In the competition for the academic position "Professor" Assoc. Prof. Dr. Iliana Apostolova participated with a total of 58 scientific publications in refereed international journals and indexed in the world-famous Web of Science and Scopus databases, including:

- **for the equivalent of habilitation work** (referring to indicator B4) Prof. Dr. Iliana Apostolova presented 11 publications published in journals with an impact factor and SJR. Divided by quartiles, they are : 5 publications in the Q2 category and 6 publications in the Q3 category.

The publications were issued in the period 2019-2023. and are related to the research of magnetically ordered, ferroelectric and antiferroelectric bulk samples and nanoscale materials.

It should be noted that in six of the publications the candidate is the first author.

- **The publications outside the habilitation work** are total of 47 (referring to indicator Г) . Divided by quartiles, they are: 4 publications in category Q1, 27 publications in category Q2, 13 publications in category Q3, 3 publications in category Q4. The publications were published in the period 2015-2023. In 19 of these 47 scientific works, the candidate is the first author.

In the framework of the competition, Assoc.Prof. Dr. Iliana Apostolova participated with 2 books, 2 University textbooks and 1 issued university handbook.

There are 414 independent citations under the competition procedure.

To date, Dr. Iliana Apostolova is a co-author in a total of 114 publications in scientific journals, of which 92 are in refereed and indexed journals from the world database Web of Science and Scopus

More than 500 citations were noted in the refereed and indexed journals from the global database Web of Science and Scopus, h - index 11 .

According to the requirements for occupying the academic position "Professor", laid down in the Law on the Conduct of the Academic Staff in the Republic of Bulgaria (ZRAS RB) and the rules for the terms and conditions for acquiring scientific degrees and occupying academic positions at the University of Forestry, the candidate. Dr. Iliana Apostolova presented:

to indicator A - 50 points (from a minimum of 50 points)

to indicator B - 190 points (from a minimum of 100 points)

to a group of indicators Г - 871 points (from a minimum of 200 points)

to indicator Д -828 points (from a minimum of 100 points)
Citations in scientific publications, monographs, collective volumes and patents - 414 points

to group of indicators E - 170 points (from minimum 1 50 points) as to them
E14. Participation in a national scientific or educational project - 90 points
E19 . Published university book or book that is used in the school network: -60 points
E20 . Published university textbook or textbook that is used in the school network: -20 points

The scientific indicators of the candidate Assoc. Dr. Iliana Apostolova fully cover the requirements for occupying the academic position "Professor" laid down in the Regulations of ZRAS RB and Forestry University-Sofia.

2. General characteristics of the candidate's scientific, scientific-applied and pedagogical activitie

Iliana Apostolova completed her Master's degree in the Department of "Solid State Physics and Microelectronics" at the Faculty of Physics, Sofia University "St. Kliment Ohridski" in 1993. In 2012, she successfully defended her PhD on the subject of "Static and Dynamic Properties of Magnetic and Multiferroic Nanoparticles" at the Faculty of Physics, Department of "Solid State Physics and Microelectronics" based on 11 publications with impact factor and impact rank. Iliana Apostolova began her career as a physics and informatics teacher at 54 Secondary School "St. Ivan Rilski", after which in 1996 she started working as an Assistant at the Forestry University, Department of "Mathematics and Physics" , as the main activity is related to leading a laboratory workshop on "Physics with the basics of biophysics", "Physics with biophysics" and "Physics ". In 2008, the candidate won a competition for Chief assistant in the Department of "Mathematics and Physics", and since the beginning of 2015 she is an Associate Professor in the Department of "Mathematics, Physics and Informatics", where she is engaged in educational and research activities .

Assoc.Prof. Dr. Iliana Apostolova is the author and co-author of 5 university books and manuals for laboratory exercises in Physics and Biophysics. Also, Prof. Apostolova is the author of a test system for assessing the knowledge of students at the Forestry University.

The textbooks are the basis of the two main courses of lectures that Associate Professor Apostolova leads at the Forestry University, and the study aid is connected with a laboratory practicum required for all students studying the disciplines of Physics and Physics with Biophysics.

Until now, Dr. Iliana Apostolova has participated in 10 research projects financed by the Scientific Research Fund and the Ministry of Education and Science.

The scientific interests of Prof. Dr. Iliana Apostolova are in the field of solid state theory and more specifically in the study of magnetically ordered, ferroelectric and antiferroelectric multifunctional materials (bulk samples and nanoscale materials). Currently, the results of the overall research activity of Dr. Iliana Apostolova are 114 publications in scientific journals, of which 92 are in refereed and indexed journals from the world database Web of Science and Scopus.

The total number of citations of Prof. Apostolova's works is over 500, noted in refereed and indexed journals from the world database Web of Science and Scopus

Prof. Apostolova holds a diploma from the journal: "Journal of Applied Physics" for the most read article: "Origin of ferromegnetism in transition metal doped BaTiO3" 113(20), 3904, 2013.

3. Basic scientific and/or scientific-applied contributions with an assessment to what extent they are the candidate's personal work.

The scientific activity of Dr. Iliana Apostolova is focused on the study of multiferroics as a wide class of materials simultaneously possessing different ferroic orderings: magnetic ordering (ferromagnetism, antiferromagnetism, ferrimagnetism, spiral structures), electrical ordering (ferroelectricity, antiferroelectricity) and/or single-phase ferroelasticity. Unlike the microscopic origin of magnetism (the same for all multiferroics), in ferroelectricity there are several microscopic sources of polarization that determine the different types of multiferroics. Prof. Dr. Iliana Apostolova has focused her academic career precisely on the theoretical study of the mechanisms for the appearance of spin-induced polarization and the clarification of the relationship between the structure and properties of multiferroics and the magnetoelectric connection, as well as the study of the effect of doping in them.

The scientific and scientific-applied contributions of Dr. Iliana Apostolova are significant and up-to-date, and find applications in medicine, electronics, instrument making, artificial intelligence and other spheres of life.

Major scientific contributions

The main scientific, scientific-applied and methodical contributions of Dr. Iliana Apostolova can be summarized in the following areas:

I. Investigation of multiferroic materials in the form of bulk samples and low-dimensional systems

1.1. Investigation of the mechanisms for the appearance of spin-induced polarization in bulk samples

A major contribution in this research area is the clarification of the relationship between the structure and properties of the studied multiferroics.

- The role of the mechanisms in the occurrence of spin-induced polarization in bulk samples of BiFeO3 and LiFeP2O7 [5, 6, 7, 29]. For example, in polar magnets such as BiFeO3 and LiFeP2O7, spontaneous polarization leads to the induction of an antisymmetric magnetic interaction [7, 29], and it has been found that below the magnetic phase transition point the spontaneous polarization depends on the ordering of the magnetic moments and can be controlled by applying a magnetic field [7, 29].
- The presence of the magnetodielectric effect was established for compounds such as LiCuVO4, LiCu2O2, CuCrO2, BiFeO3, AgCrS2, AgCrO2, Ca3Mn2O7, etc. The dependence of the magnitude of the detected peak has been studied in the temperature dependence of the dielectric constant at the point of magnetic phase transition and its position on the magnitude and direction of the applied external magnetic field, taking into account the spin-phonon interaction [3, 10, 23, 27, 33, 34]. The absence of a peak in the dielectric constant in the absence of a magnetic field and the decrease in its value when a magnetic field is applied has been interpreted as the appearance of antiferroelectric ordering in Li2ZrCuO4 [4] and NaCu2O2 [31].
- The possibility of the appearance of multiferroic properties in compounds with antiferroelectric-antiferromagnetic arrangement in one phase at Cu2O2(SeO3)4Cl6 has been theoretically proven [32]. When examining the dependence of the polarization on an external electric field, a double hysteresis dependence and the appearance of spontaneous magnetization upon application of an electric field were observed.
- Different mechanisms for spin-induced polarization or its absence have been established in compounds of the type AgCrS2 and AgCrO2, LiFeP2O7 and LiCrP2O7, NaCu2O2 and LiCu2O2, which are structurally isomorphic, but their different chemical composition gives rise to different interactions [27, 29, 31].

1.2 . Investigation of the doping effect and creation of low dimensional systems

Dr. Apostolova chooses the method of doping as a way to change the structural parameters of the crystal lattice, causing contraction and stretching processes, changes in the magnetic and electrical ordering and the relationship between the two ordering parameters. Doping with ions of the same valence or a different valence than that of the substituted ions has been selected. The case of creating anion vacancies in order to ensure charge neutrality was also investigated.

- A model was created [1] describing the changes in the multiferroic properties of $BaTiO_3$ nanoparticles doped with ions from the transition metal group (for example, with Fe ($BaTi_{1-x}Fe_xO_3$)). It was established that in undoped $BaTiO_3$ nanoparticles, the occurrence of ferromagnetism is due to the presence of oxygen vacancies on the surface, which leads to the appearance of Ti^{3+} and/or Ti^{2+} with non-zero spin. In the case of Fe doping ($BaTi_{1-x}Fe_xO_3$), the simultaneous presence of Fe^{3+} and Fe^{4+} ions leads to a new mechanism responsible for the occurrence of ferromagnetism. The

ferromagnetic Fe^{4+}–Fe^{4+} interaction was found to dominate over the antiferromagnetic Fe^{3+}–Fe^{3+} and Fe^{3+}–Fe^{4+} interactions, leading to a significant increase in magnetization. Through numerical calculations, Assoc. Prof. Apostolova proves that the magnetization and the temperature of the magnetic phase transition increase with doping, while the polarization and temperature of the ferroelectric transition decrease.

- The changes of ferromagnetism in nanoparticles of $BaTiO_3$ doped with rare earth elements (for example Er), which replaces Ba-ions- $Ba_{1-x}Er_xTiO_3$, were analyzed. The dependence of the value of the dielectric constant on the applied external magnetic field has been proven[22].
- It was found that when $YCrO_3$ is doped with Mn-ions (replace Y), the dielectric constant increases with increasing degree of doping, and when doped with Gd, it decreases [20]. The obtained results are explained by the difference in the ionic radii of the doping elements compared to the radii of the substituted Y-ions. Such conclusions were also made for $LaFeO_3$ [25], by replacing the magnetic Fe-ions with transition metal ions.
- The difference in the polarization behavior in isomorphic compounds $LuFeO_3$ and $LaFeO_3$ when doped with Sm, which replaces the non-magnetic Lu(La)-ions, was analyzed [43]
- The effects of doping a compound with the same chemical composition but a different crystal structure for a structural phase transition from orthorhombic to hexagonal crystal lattice when doping $YFeO_3$ with Sc, which replaces Fe-ions, have been established [41].
- It has been proven that the appearance of a structural phase transition upon doping of $BiFeO_3$ nanoparticles with Tb is responsible for an increase in the spin-induced polarization in the system [45].

II. Scientific and applied contributions

2.1. Establishment of "room-temperature magnetism" and "room-temperature multiferroism" in doped magnetic and multiferroic nanoparticles [9, 12, 13, 16, 21 , 30 , 37, 38, 40, 44, 46, 47]

Prof. Apostolova has studied in detail the change in the properties of magnetic nanoparticles by changing the shape, size and/or controlled change of their composition by introducing impurities into magnetic and multiferroic compounds. The presence of the so-called "room-temperature magnetism" and "room-temperature multiferroism" open vast applications in spintronics, optoelectronics and medical physics.

- Nanoparticles of undoped compounds such as SnO_2, In_2O_3, $CuAlO_2$, FeS_2, $Bi_2Fe_4O_9$ and Fe_3O_4 have been found to exhibit macroscopic magnetization at room temperature, which is absent in bulk samples [9, 13, 21, 38, 46, 47]. A qualitative explanation has been proposed for the appearance of magnetic ordering at room temperature in the case of SnO_2 [9] and In_2O_3 [13], related to the appearance of anion vacancies.

- The occurrence of magnetization in non-magnetic nanoparticles of FeS_2 NPs [21] has been established, as a consequence of the appearance of a FeS magnetic phase with sulfur vacancies, and as the size decreases, the magnetization increases. The appearance of a magnetically ordered state at room temperature in $CuAlO_2$ [38] is related to the appearance of uncompensated spins of Al^{3+} ions.
- Numerical calculations of the occurrence of magnetization during substitution doping in SnO2, TiO2 and CeO2 disordered magnetic semiconductors with non-magnetic impurities, magnetic ions of transition metals or rare earth elements are presented [9, 12, 16]. It has been established that the influence of impurities is different, and upon doping the magnetization can increase, decrease or pass through a maximum.
- It was established that upon doping of SnO_2 [9], TiO_2 [12] and CeO_2 [12] nanoparticles with Co^{2+} ions (transition metal), the radius of which is smaller than that of Sn^{4+}, Ti^{4+} and Ce^{4+} -ions, a contraction voltage is detected, which is the reason for the appearance of magnetization. At low concentrations of impurity atoms, with an increase in the degree of doping due to the $s-d$ interaction, the magnetization increases, reaching a maximum. Further increase in the impurity concentration leads to a decrease in the magnetization (related to the appearance of an over-exchange interaction between the localized Co-spins, which is antiferromagnetic) .
- It was established that when doping SnO2, TiO2 and CeO2 nanoparticles with ions of rare earth elements (such as Pr^{3+} and Sm^{3+} ions) [16] with an increase in the concentration of impurity ions, the magnetization in SnO2, TiO2 and CeO2 decreases in comparison to undoped samples.
- A decrease in the magnetization and the temperature of the magnetic phase transition was observed when Fe_3O_4 nanoparticles were doped with rare earth element Gd^{3+} [47]. It was found that Gd^{3+} ions replace Fe-ions in octahedral positions and due to their larger radius, stretching stresses appear, which leads to a decrease in the magnitude of interaction between Fe spins. In addition, Fe-magnetic moments and spins of Gd-ions are antiferromagnetically positioned, resulting in two effects leading to a decrease in the macroscopic magnetization in doped magnetite. The dependence of the magnetization of $CuCr_2O_4$ nanoparticles upon doping with rare earth Pr was interpreted similarly [37].

2.2. Self-consistent magnetic hyperthermia [11, 18, 24, 28, 36, 42]

Part of the scientific and applied contributions of Prof. Apostolova are focused on the study of magnetic hyperthermia - an innovative method of fighting cancer, consisting in local heating of malignant formations, which leads to their destruction, while preserving healthy cells. The heating effect is achieved with the use of magnetic nanoparticles, which when interacting with an alternating magnetic field "produce" a heat. The main problem in this therapy is the monitoring of the temperature field around the tumor, and the innovativeness in the scientific and applied activities of Prof. Apostolova is precisely in its solution.

- The use of magnetic nanoparticles with a magnetic phase transition temperature from a magnetically ordered to a magnetically disordered state in the critical temperature interval of 41°C to 46°C has been proposed. Above this temperature, the

nanoparticles go into a paramagnetic state and the heating process stops, resulting in self-controlled magnetic hyperthermia.

- The so-called specific absorption rate coefficient has been proposed that measures the absorbed thermal power, normalized to the mass of the magnetic nanoparticles, since the heating process is associated with hysteresis losses
- The effect of nanoparticles has been established for "in vivo" and "in vitro" applications with a magnetic phase transition temperature in the interval between 41°C and 46°C [11, 18, 24, 28, 36, 42]. This temperature is achieved by changing the nanoparticle size, type and degree of doping [11, 18, 28, 36, 42]. For example, for compounds of the type $La_{1-x}Sr_xMO_3$ [11], $Me_{1-x}Zn_xFe_2O_4$ with Me=Co,Ni,Cu,Mn [18] and $Y_3[Fe_{2-y}M_y]_a(Fe_{3-z}M_z)_dO_{12}$ with M=Al,Ga,Sc,In [36] are certain magnetic nanoparticles that have optimal parameters and are biologically friendly to the human organism.
- It was found that the size of the magnetic nanoparticles needed to be less than 25 nm, which provided the possibility of transport through capillary blood vessels; non-toxicity and biocompatibility; and that the magnetic field created is biologically safe and within human pain tolerance.

3. Methodical contributions

3.1 . Issued textbooks and study books

Prof. Dr. Iliana Apostolova is the author and co-author of 5 university books and manuals for laboratory exercises in physics and biophysics. The books are the basis of the main lecture courses leaded by Prof. Apostolova at the Forestry University. The student test guide issued is linked to a laboratory practicum required for all students studying Physics and Physics with Biophysics.

From the documents attached to this competition, it is clear that Assoc. Prof. Dr. Iliana Apostolova is a well-established professional in the field of research of multiferroic properties of bulk samples and nanomaterials and has an essential role in publishing the experimental results obtained so far in the articles attached to the competition, as well as is recognizable among the scientific community (citations). Assoc. Prof. Dr. Iliana Apostolova has an active teaching activity, she is an author and co-author of 5 university books and manuals for laboratory practicum in physics and biophysics.

4. Reflection of the candidate's scientific publications in our and foreign literature:

The indicated citations to the scientific publications with which the candidate participated in the competition according to Web of Science and Scopus are 414.

The total number of independent citations of all scientific publications of the candidate are over 500.

5. Critical notes of the reviewer on the presented works, including the candidate's literary awareness

I have no critical notes.

6. Personal impressions of the reviewer about the candidate

I do not know Assoc. Prof. Dr. Iliana Apostolova personally, but I am extremely impressed by the huge variety of multiferroic materials that she has extensively investigated. Dr. Iliana Apostolova successfully found the connecting thread in the mechanisms of spin-induced polarization and the relationship between structure and properties at the macroscopic level by defining of microscopic Hamiltonians describing the behavior of the electric and magnetic subsystems and the relationship between them.

I believe that her scientific and research activities are impressive and the proof of this is the numerous publications in renowned journals such as J. of Alloys and Compounds; J. of Magnetism and Magnetic Materials; Physica E; Materials Today Commun. and others , as well as the large number of noticed citations. Last but not least is her teaching activity.

Also, the attached tender documents are excellently organized. All this gives me a reason to believe that Assoc. Prof. Dr. Iliana Apostolova is an exceptional professional in her field and a very valuable member of any scientific team.

7. Reasoned and clearly formulated conclusion.

The materials and scientific works of Assoc. Prof. Dr. Iliana Apostolova presented in this competition characterize the candidate as an excellent qualified specialist.

Here I would also like to note the active participation of Assoc. Prof. Dr. Iliana Apostolova in many research projects.

The above data show that the scientific indicators of Prof. Dr. Iliana Apostolova fully satisfy the requirements for occupying the academic position "Professor" laid down in the Law on the Regulation of the Academic Staff in the Republic of Bulgaria (ZRAS RB) and the regulations on the terms and conditions for acquiring scientific degrees and occupying academic positions of Forestry university, Sofia.

On the basis of above, I express my full support for the application of Assoc. Prof. Dr. Iliana Apostolova and with conviction I recommend to the honorable Scientific Jury to support and propose to the National Assembly of the Forestry University that Assoc. Prof. Dr. Iliana Apostolova to be elected to the academic position " Professor" to Professional direction: 4.1. Physical sciences.

10/04/2024

Written by the reviewer:

/Prof. DSc Marin Gospodinov /