Appendix 12b

REPORT

of dissertation for the acquisition of:

educational and scientific degree " **doctor** "	X
scientific degree **"Doctor of Science"**	
	the true is indicated by the sign "X"

Author of the dissertation:

		Martin	Rosenov	Pernikov	UCTM
academic position	scientific degree	name	middle name	last name	workplace

Topic of the dissertation:

"Synthesis, microstructure and electrical properties of oxide glass ceramics"

Scientific area:

4	Natural sciences, mathematics and informatics
code	name

Professional area:

4. 1.	Physical sciences
code	name

Scientific specialty:

Electric, magnetic and optical properties of condensed matter

The report was written by:

Associate Professor	Dr.	Margarita	Kirilova	Milanova	Institute of General and Inorganic Chemistry-BAS
academic position	scientific degree	name	middle name	last name	workplace

1. Meeting the minimum requirements under the Regulations:

A) The candidate meets the minimum requirements	20 points	X
B) The candidate doesn't meet the minimum requirements	0 points	
		one of the answers given is marked with the sign "X"

It is mandatory to fill in if answer B is marked. The publication activity of the candidate is analyzed. The response of the results achieved (quoted) is analyzed.

2. The relevance of the topic of the dissertation:

A) The topic is relevant and new (there are no known results on the topic by other authors)	8 points	
B) The topic is relevant and results from other authors are known	6 points	X
C) The topic is not relevant, but results from other authors are known	2 points	
D) The topic is not relevant and no results from other authors are known	1 point	
E) The topic does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign ""

The evaluation of the relevance of the dissertation must be substantiated
The topic of the dissertation is interesting and relevant, as it is related to research on the synthesis, morphological and electrical characteristics of glass ceramics containing the barium titanate ($BaTiO_3$) phase. This phase, as well as materials based on it, have been the subject of intensive research for decades, as they are known to possess excellent dielectric, ferroelectric, and specific optical properties. In particular, glass ceramics containing the barium titanate ($BaTiO_3$) phase derived from oxide glasses are promising candidates for the production of low-cost materials with controllable dielectric properties for energy storage, which is becoming an increasingly important task nowadays. In addition to being an environmentally friendly and low-cost material in energy storage, barium titanate-based glass ceramics can be applied as part of magnetic (if there are additives that lead to magnetic properties) or resistive sensors, as device components for microwave applications, and in components of solid oxide fuel cells operating at medium and high temperatures. In the theoretical part of the dissertation, a literature review was made of the main methods for obtaining the two most commonly used polymorphic modifications of $BaTiO_3$ - tetragonal and cubic, as well as modified barium titanate glass ceramics. Some unresolved questions related to the phase composition, microstructure and dielectric properties of glasses and glass-ceramics in the $NaO/Al_2O_3/BaO/TiO_2/B_2O_3/SiO_2/Fe_2O_3$ system, in which controlled crystallization of $BaTiO_3$ and Fe-containing $BaTiO_3$ is possible, are indicated, as well as the preparation of glass ceramics containing solid solutions of $Ba_{1-x}Sr_xTiO_3$ by partial replacement of BaO with SrO. The clarification of these questions determines the main goal of the dissertation, the achievement of which will lead to obtaining important information of a fundamental and applied nature, and will contribute to expanding the fields of practical application of the obtained materials.

3. Type of research:

A) Theoretical	4 points	
B) Applied	4 points	
C) Theoretical with application elements	4 points	X
D) It does not correspond to the level of dissertation	0 points	
		one of the answers given is marked with the sign "X"

The level of research must be substantiated if answer D is marked.

4. Objectives of the research:

A) Realistic and of scientific and / or applied interest	8 points	X
B) Realistic, but not of scientific and / or applied interest	3 points	
C) Unattainable (unrealistic)	0 points	
		one of the answers given is marked with the sign "X"

Objectives must be specified. The type of the set objectives must be justified.
The main goal of the dissertation is the synthesis and investigation of the dielectric properties of modified perovskite-based barium-titanate glass-ceramics obtained from oxide glasses. More specifically, the work aims to study the influence of the chemical and phase composition, as well as the microstructure, on the dielectric and magnetic properties of glass ceramics based on barium titanate with nano- and submicron crystallite sizes. The goal is clearly and well formulated and has a fundamental-applied character, since its achievement will lead to obtaining new materials and new data on the composition-structure-properties relationship. In order to achieve the goal thus set, several general and specific tasks have been formulated, which outline a well-planned and targeted research.

5. Contributions of the dissertation:

A) With lasting scientific and / or applied response, they form the basis for new research and applications	20 points	X
B) They are of significant scientific and / or applied interest, complete and / or summarize previous research	16 points	
C) They are of scientific and / or applied interest	12 points	
D) Lack of significant contributions	8 points	
E) Lack of contributions	0 points	
		one of the answers given is marked with the sign ""

Contributions must be specified. The type of results achieved must be justified.
The contributions can be summarized as follows. 1. New compositions of oxide glasses with a high content of alkali and alkaline earth oxides have been proposed, in which it is possible to obtain a dielectric phase with a high volume fraction. 2. The main physico-chemical properties of the obtained glasses - temperatures of glass formation and crystallization, basic structural units in glasses and the glass ceramics, the phase composition and morphology of the obtained glass ceramics have been established and hypothesis about the presence of phase separation in them, which precedes the process of controlled crystallization have been proposed. 3. A complex characterization of the thermophysical and mechanical properties of the resulting glasses and their interrelationship is established. 4. The mechanism of electrical conduction in the obtained glasses and glass-ceramics is established and their areas of potential applicability are outlined as dielectrics in multilayers capacitors, parts of sensor and opto-electronic systems. The contributions of the present dissertation are of a fundamental nature and refer to the selection of new compositions of multicomponent oxide glasses in order to obtain glass-ceramics with applications in electronics and sensor technologies and the characterization of their structure, phase composition and physical properties. Special attention is paid to the study of the electrical properties of the obtained glasses and glass-ceramics. The most important results obtained can be summarized as follows:

1. New compositions of glasses and glass ceramics were synthesized in the systems $NaO/BaO/SrO/TiO_2/B_2O_3/SiO_2/Al_2O_3$ and $NaO/BaO/SrO/TiO_2/B_2O_3/SiO_2/Al_2O_3/Fe_2O_3$ containing different amounts of SrO (0.5, 1, 3 , 6 and 9 mol%) at the expense of BaO at fixed Al_2O_3 concentrations of 0 and 3 mol%.
2. Through controlled crystallization of the synthesized glasses, glass ceramics containing $BaTiO_3$ and/or $Ba_{1-x}Sr_xTiO_3$ as main crystalline phases are obtained.
3. Through SEM analysis, it was found that the crystals contain Ba, Ti, Sr, Fe. It was found that the average size of the crystalline particles in the glass-ceramics increases with increasing time and temperature of thermal treatment. In the system containing iron oxide, the resulting crystals are as a rule smaller than those in the non-iron containing system.
4. By the computer microtomography method of selected glass ceramics from the system $(23.1-x)Na_2O/17{,}1BaO/6SrO/23TiO_2/7.6B_2O_3/17.4SiO_2/xAl_2O_3/5.8Fe_2O_3$ it was established that with increasing concentration of aluminum oxide the average size of of barium titanate crystals increases and their volume content also slightly increases.
5. IR and Raman spectroscopies proved that in glass ceramics from the systems $20.1Na_2O/(23.1-y)BaO/ySrO/23TiO_2/7.6B_2O_3/17.4SiO_2/3Al_2O_3/5.8Fe_2O_3$ with different concentrations of SrO – = 0.5, 1, 2, 3, and 6 mol % SrO- has barium or barium-strontium titanate, and also the presence of various silicon- or boron-containing structural units (mainly based on Si_{O4} tetrahedra and BO_3 triangles), the amounts of which depend on the SrO content and Al_2O_3.
6. Through impedance spectroscopy, it was established that the obtained glasses and glass ceramics are insulators at room temperature (resistance values of the order of 10^8 Ohms). For the glass ceramics with 6 mol% SrO, 2 or 3 phase transitions are observed for the barium-strontium titanate above room temperature. For temperatures lower than room temperature, no phase transitions are observed.
7. The dielectric constants of glasses and glass ceramics have been determined and are of the order of 40 at 100 kHz at room temperature. This relatively small value of the dielectric constant is attributed to the crystallization of cubic barium-strontium titanate.
8. In the obtained glasses and glass-ceramics, it can be assumed that the conductivity takes place in a "dielectric phase in an ionically conductive glass matrix" system, i.e. through the glass phase and by directed movement of sodium ions.
The results thus obtained have a fundamental-applied character, as they are related to the preparation of new compositions of glasses and glass ceramics with dielectric properties and to the clarification of the relationship composition-structure-properties of the obtained materials.

6. Conclusion

A) The evaluation of the dissertation is **POSITIVE**	This evaluation is assigned to a total number of at least 40 points	X
B) The evaluation of the dissertation is **NEGATIVE**	This evaluation is assigned to a total number below 40 points	
		one of the answers given is marked with the sign "X"

To be filled in at the request of the member of the scientific jury

In conclusion, I believe that the presented dissertation work is a well-argued, planned and conducted scientific research. The set goal has been successfully achieved and they are obtained a large volume of interesting mutually supporting results in the field of oxide glasses and glass-ceramics with the potential for application in electronics, which represent an original contribution to science and meet the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (ZRASRB).
The doctoral student has in-depth theoretical knowledge and professional skills in the scientific specialty Electric, magnetic and optical properties of condensed matter, which would allow him to conduct independent scientific research.
Due to the above, I confidently give my positive rating for the research conducted, represented by a dissertation, an abstract, achieved results and contributions, and I propose to the honorable scientific jury to award the educational and scientific degree "doctor" of Martin Rosenov Pernikov in the scientific field

"Natural sciences, mathematics and informatics", professional direction 4.2.Physical sciences, scientific specialty “Electrical, magnetic and optical properties of condensed matter”.

	The report was written by:	
17.06.2024	**Assoc.prof. Dr. Margarita Milanova**	signature