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Ceramics with adjustable dielectric properties based on the system SrO – TiO_2 – SiO_2

Abstract. *This work presents the results of optimization of the compositions area of radio-absorbing ceramic. As a result of laboratory samples test, dependences "composition – property" was obtained, the choice of the most technologically advanced composition area and sintering temperature for manufacturing the radio-absorbing ceramic was substantiated. The optimal composition of the Sr- titanate ceramics is characterized by the following properties: water absorption (W = 1,3 %), dielectric permeability (ε = 115), density (ρ =4,35·10^3 kg/m^3).*

Streszczenie. *W pracy przedstawiono wyniki optymalizacji powierzchni kompozytowej materiałów ceramicznych pochłaniających fale radiowe. W wyniku badań laboratoryjnych próbek uzyskano zależności "kompozyt - właściwość", uzasadniono wybór najbardziej technologicznie zaawansowanej powierzchni kompozytowej oraz temperatury spiekania dla wytwarzania materiału ceramicznego pochłaniającego fale radiowe. Optymalny ceramiczny kompozyt strontowo-tytanowy charakteryzuje się następującymi właściwościami: absorpcja wody (W = 1,3 %), przenikalność dielektryczna (ε = 115), gęstość (ρ =4,35·10^3 kg/m^3).* ***Ceramika o regulowanych właściwościach dielektrycznych w oparciu o system SrO-TiO_2-SiO_2***

Keywords: radio-transparent materials, radio-absorbing materials, strontium titanate, synthesis and firing temperature dielectric permeability, water absorption.
Słowa kluczowe: radio-transparent materiały, radio-absorbing materiały, tytanian strontu, syntezy i temperatury wypalania przenikalność dielektryczna, absorpcja wody.

Introduction

It is known that radio-absorbing materials (RAM) are structural dielectrics that effectively absorb the electromagnetic energy of radio waves [1, 2].

According to the classification, radio-absorbing materials can be magnetic and non-magnetic. In turn, non-magnetic radio-absorbing materials are subdivided into gradient, interference and combined [3].

Gradient RAM have a multilayer structure (see Figure 1) with a smooth change of the value of dielectric permeability along the thickness of the material $\varepsilon_1 > \varepsilon_2 > \varepsilon_3 > \varepsilon_n$. The first layer of RAM should be made of a material having low dielectric losses (ε_1) in order to match the wave resistance of air and material. Other layers are made of solid dielectrics with high dielectric permeability (ferroelectrics, ferroelectromagnets and others), and also with the use of magnetic or non-magnetic radio-absorbing fillers, which are introduced into the dielectric matrix (graphite, ferrites and others) [4, 5].

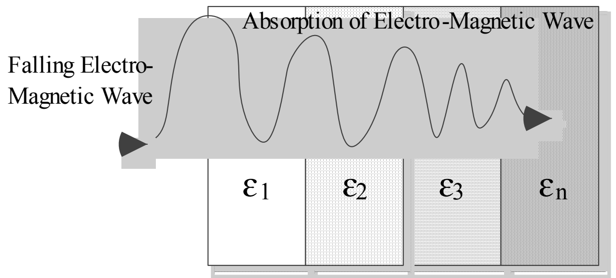

Fig. 1. Schematic view of the gradient radio-absorbing material

As the dielectric materials (the first layer of gradient RAM), which have low values of the dielectric properties, radio-absorbing materials can be used. For example, the dielectric permeability of sitalls varies no more than ± 1%, and the tangent of the dielectric loss angle varies no more than ± 20% while the temperature is changing from – 60 to +1200 ° C [6].

One of the crystalline phases, which is characterized by low dielectric properties and simultaneously by high mechanical properties in a wide frequency range of radio waves, is strontium anorthite. This crystalline phase, except a low value of the dielectric permeability, has the lowest dielectric loss from the number of crystalline phases used in the creation of radio-ceramic products [7-9].

The authors [10] developed a ceramic material that can be used as the first layer of a graded RAM and which is characterized by low values of the dielectric properties: dielectric constant ε = 4 – 6 and the tangent of the dielectric loss angle tgδ = 0.05-0.015 in the microwave range of 26 – 37.5 GHz.

Ceramics based on strontium titanate is perspective for creating a second and subsequent layer of a gradient radio-absorbing material (see Figure 1) due to the relatively low and practically constant value of the dielectric permeability and the tangent of dielectric loss angle in the broad frequency range of radio waves compared to other crystalline phases (see Tables 1 and 2).

Table 1. Properties of compounds with high dielectric losses

Compound	Structure type	ε_r at 20 °C and 1 MHz	$10^4 \cdot tg\delta$ at 10^6 Hz and 20 °C	The sintering temperature, °C
TiO_2	Rutile	90	10	1460
$SrTiO_3$	Perovskite	155	1*	1600
		250	3**	
$BaZrO_3$	Perovskite	38	–	1800
$MgTiO_3$	Ilmenite	14	3	1460
Mg_2TiO_4	Spinel	14	3	1460
$NiTiO_3$	Ilmenite	18	4	1500
$SrZrO_3$	Perovskite	30	5	1600
$SrSnO_3$	Perovskite	18	5	1700
$BaTiO_3$	Perovskite	>1000	5	1600

* – according to B.N. Vul
** – according to Yu.V. Koritsky

The relevance and work in a whole consists in the development of new compositions of ceramic materials based on the crystalline phase of strontium titanate with adjustable dielectric properties based on the three-component system SrO – TiO_2 – SiO_2 for the effective gradient RAM creation.

Table 2. Frequency dependence of the dielectric permeability and the tangent of the dielectric loss angle of strontium titanate

Compounds	Properties	Parameter values at frequency, Hz				
		10^2	10^4	10^6	10^8	10^{10}
Strontium titanate $SrTiO_3$	ε	234	232	232	232	230
	$10^4 \cdot tg\delta$	21	8	2	1	28

Analysis of literary data and the formulation of the problem

The problem of synthesis of strontium titanate with adjustable values of the dielectric permeability is investigated by scientists from many countries, using various methods. Works on the study of ceramics with high dielectric permeability were initiated by the outstanding scientists A.F. Ioffe, G.I. Skanavi, I.V. Grebenshchikov, B.N. Vul, and others.

The authors [11] developed new ceramic compositions with high values of dielectric permeability on the basis of strontium titanate with the addition of a new component BiMO3, where M is chromium, manganese or iron, through the introduction of which, new materials with high dielectric permeability are obtained. The dielectric permeability of such materials is in the range from 141 to 530 at a radio wave band of 0.5 – 2 GHz.

In this work [12] the effect of creating the material with a high dielectric permeability on the basis of strontium titanate (stoichiometric composition) barium zirconate and solid solution of $(BaZn)TiO_3$ is demonstrated. However, these works are aimed at creating materials based on the stoichiometric composition with a higher dielectric permeability ε = 380.

Investigation of creating process of ceramic materials with high dielectric permeability values was carried out in the work [13] and it was established that the insertion of Nb_2O_5 impurity into strontium titanate makes it possible to obtain ceramic materials with the following properties: ε = 1350 at 100 MHz and ε = 450 at 1 GHz.

The authors [14] established the effect of the type of crystal lattice on the value of dielectric permeability of titanates of beryllium, calcium, strontium and barium of stoichiometric composition. It is showed that a perovskite-type crystal lattice contributes to obtaining large values of the dielectric permeability. With the ionic radius of alkaline earth metals in perovskite-type crystal lattices increasing, the distance between ions also increases, that leads to decreasing of the bonds' strength among them, e.g. it leads to greater polarization and, consequently, to the dielectric permeability increasing. In practice, it has been established that the value of the dielectric permeability of strontium titanate is 150, and for barium titanate it exceeds 1000.

Thus, it is expedient to carry out the research of new ceramic compositions development based on the crystalline phase – strontium titanate, which were characterized by dielectric permeability within a wide range from 100 to 150 and to study the dielectric and physical properties, microstructure and phase composition of these materials.

Goals and objectives of the study

The aim of the research was obtaining a ceramic material with adjustable dielectric properties on the basis of the $SrO – SiO_2 – TiO_2$ system by developing new ceramic compositions that are in the crystallization domain of strontium titanate.

To achieve this goal, the following tasks were set:

- to develop new compositions of ceramics with adjustable dielectric properties;
- to investigate the effect of the strontium titanate synthesis temperature and the firing temperature on the mechanical and dielectric properties of ceramics and study its phase composition and microstructure.

Research Methods

Synthesis and firing of samples in a laboratory muffle furnace Nabertherm HTCT 01/16 at temperatures 1330 – 1430°C with holding from 1 to 2 hours were implemented.

Determination of dielectric properties was carried out on immittance meter E 7–8 according to GOST 24409-80. Using the measured values of the electrical capacity of the samples, the dielectric permeability was determined. The calculation was based on the formula for determining the electrical capacity:

$$\varepsilon = \frac{C \cdot d}{\varepsilon_0 \cdot \pi \cdot r^2}, \quad (1)$$

where C – is the measured value of the electrical capacity of the sample, d – is the thickness of the sample, ε_0 – is the dielectric permeability, and r – is the radius of the electrodes.

Determination of the apparent density, water absorption and open porosity of the test samples was carried out by the hydrostatic weighing method in water in accordance with GOST 24409-80.

Investigation of the morphological features of the fracture surface of the samples with scanning electron microscopy (SEM) method using a scanning electron microscope JSM-6390LV (JEOL, Japan) was carried out. These studies were performed in the secondary electron regime with an accelerating voltage of 10–20 kV and a small beam current.

The phase composition of the test samples using the X-ray phase analysis (XRD) method was determined. X-ray diffractograms on a DRON-3M diffractometer with CuKα − radiation and a nickel filter under constant operating conditions were taken. To identify the phases, the American card index ASTM was used.

New compositions of ceramics with adjustable dielectric permeability

At the preliminary stage of the research we carried out a theoretical analysis of thermodynamic reactions and for the first time a phase diagram of the three-component system $SrO – TiO_2 – SiO_2$ was constructed [15] (see Fig. 2).

To develop new compositions of ceramics with adjustable dielectric properties, the compositions that are in the region of crystallization of strontium titanate $SrTiO_3$ were studied. The composition "I" corresponds to the stoichiometric composition of strontium titanate; composition "II" is located in the elementary triangle Sr_3T_2 – SrS – SrT; composition "III" is located in the elementary triangle SrT – SrS – SrTS; composition "IV" is located in the elementary triangle SrT – SrTS – T (see Table 3). Shows the figurative points of the research contributions of ceramics are shown at the Fig. 2.

Table 3. Chemical composition of experimental masses

Code of composition	Oxides content, wt. %		
	SiO_2	TiO_2	SrO
I	-	43.48	56.52
II	1.97	45.4	52.63
III	3.95	46.05	50
IV	3.947	51.316	44.737

For the production of ceramic materials, the following raw materials were used: strontium carbonate, titanium dioxide and sand quartz Vishnevetsky. The chemical and charge composition of the masses are given in Table 4.

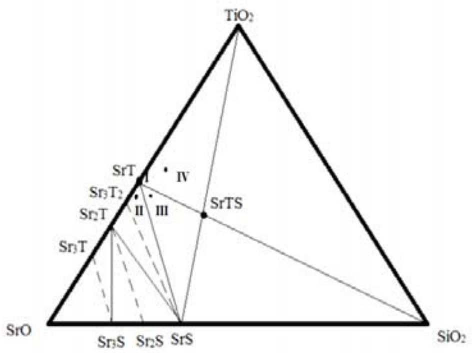

Fig. 2. Diagram of the state of the three-component system SrO – TiO_2 – SiO_2 [15]

Table 4. Chemical composition of raw materials

Raw materials	Content of components, wt. %						
	SiO_2	TiO_2	SrO	Al_2O_3	Fe_2O_3	CaO	V.p.p.
Quartz Vishnevetsky	99.35	-	-	0.421	0.06	0.039	0.13
Titanium Dioxide	-	100	-	-	-	-	-
Strontium Carbonate	-	-	69.49	-	-	-	30.51

Technology for obtaining prototypes

To study the influence of the firing temperature on the dielectric properties of researched ceramic samples, the compositions of ceramics "I", "II", "III" and "IV" were taken (see Fig. 2).

The technology of manufacturing ceramics based on strontium titanate is two-staged one. The first stage was a synthesis of strontium titanate with thoroughly mixed dry components of the raw materials of Vishnevetsky quartz, titanium dioxide and strontium carbonate at temperatures of 1300, 1350 and 1400 °C in the Naberterm HTCT 01/16 muffle furnace in an oxidizing medium with holding at a maximum temperature of 2 hours. The synthesis of strontium titanate was accompanied by a large shrinkage due to the dissociation of strontium carbonate ($SrCO_3$). Further, grinding of synthesized strontium titanate was carried out, followed by the formation of test samples by semi-dry pressing. The firing temperature of the prototypes in the second stage was 1330, 1380 and 1430 °C, respectively, with holding at a maximum temperature of 1 hour.

The produced samples after firing were examined for water absorption, apparent density, open porosity and dielectric permeability.

The results of research on the properties of ceramics

The results of determination of water absorption, open porosity, density and dielectric permeability as a function of the firing temperature of the test samples are shown in the Table 5.

The obtained results indicate that the best composition is the non-stoichiometric composition "II" burned at a temperature of 1330 °C with following properties: dielectric permeability 115, water absorption 1.3%, open porosity 5.8% and density $4.35 \cdot 10^{-3}$ kg /m^3, which fully corresponds to the stated goal of our study. We have established that as a result of high-temperature deformation, it is impossible to study dielectric properties for compositions III and IV burnt at temperatures of 1380 and 1430 °C. As for the other compositions studied, the necessary crystalline phase, i.e., strontium titanate, is not formed in the proper amount, and titanium dioxide is present in the free form, as the values of dielectric properties of the prototypes indicated in a range from 42 to 98.

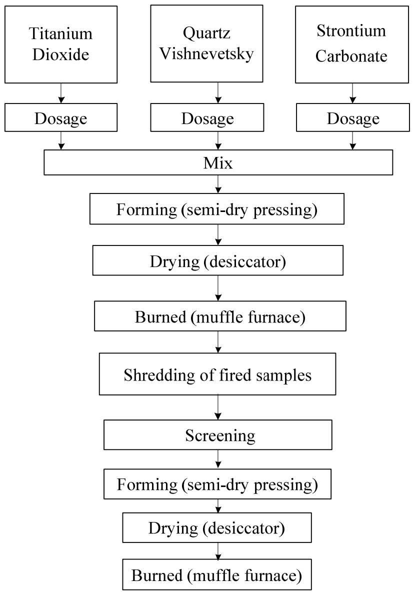

Fig. 3. Technological scheme for production of prototypes

Table 5. Dependence the studied ceramics properties on the firing temperature

Number of composition	Temperature °C,	Water-absorption W,%	Open porosity P, %	Density $\rho \cdot 10^{-3}$, kg/m^3	Dielectric permeability, ε, 1 kHz
I	1330	6.0	22.4	3.71	80
II		***1.3***	***5.8***	***4.35***	***115***
III		1.1	4.6	4.14	60
IV		1.1	4.4	4.05	73
I	1380	5.7	21.7	3.8	64
II		0.44	2.0	4.5	72
III		0.44	1.9	4.22	79
IV		0	0	3.99	- *
I	1430	5.7	21.4	3.74	98
II		0.2	1.1	4.40	86
III		0	0	4.37	- *
IV		2.1	8.9	4.19	42

* – samples melt during firing

Using the X-ray phase analysis of the "II" sample composition burnt at a temperature of 1330 °C (Fig. 4), the completeness of the reactions of strontium titanate formation was investigated, and the phase composition of the heat treatment products was determined. The bar-radiograph shows strontium titanate and insignificant peaks of TiO_2 and Sr_2SiO_4, which indicates the completeness of the crystalline phase of strontium titanate formation.

The results of scanning electron microscopy of the sample "II", scorched at a temperature of 1330 °C (see Fig. 5), indicate that the structure is compacted with the addition of silicon oxide. This affects the maximum size of the crystals, which reach a size of 10 microns. In general, the crystal sizes range is from 0.5 to 2 μm, and the pores reach 5 μm in the regions of recrystallization.

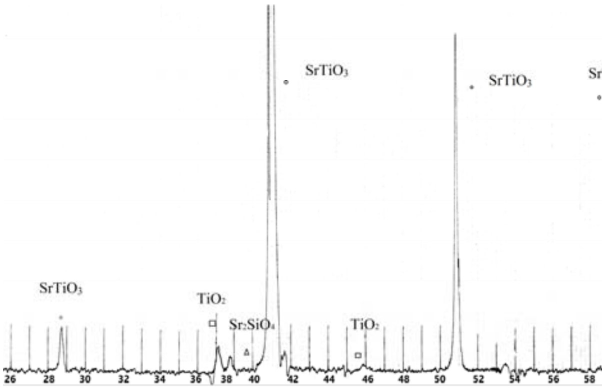

Fig. 4. Bar-radiograph of the sample "II" (firing temperature 1,330 °C)

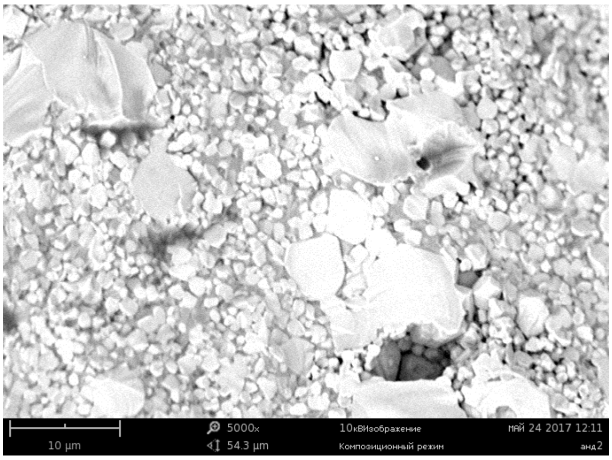

Fig. 5. Microstructure of the ceramics of the composition "II" (firing temperature 1330 °C)

So, after the conducted researches, it is possible to draw a conclusion that in the future there are prospects for studying the state of the system $SrO – TiO_2 – SiO_2$ for the development new ceramic materials with high dielectric and physic mechanical characteristics.

Conclusions

The work done allowed to solve the problem of obtaining a ceramic material based on the $SrO–Al_2O_3–SiO_2$ system with high values of the permeability.

On the basis of the studies carried out, a technology for manufacturing a ceramic material of composition «II» with a high dielectric permeability was developed. The technology of manufacturing ceramics based on strontium titanate consisted of two stages. The first stage of synthesis occurred at a maximum temperature of 1300 ^oC with holding during 2 hours. The second stage was carried out at a temperature of 1330 ^oC with holding for 1 hour.

It was found that the composition "II" has the best indicators (firing temperature 1330 °C), which is located in the triangle Sr_3T_2 – SrT – SrS with the following properties: dielectric permeability ε = 115; water absorption W,% – 1.3; open porosity P% –5.8; density ρ, g / cm^3 – 4.35.

The generalization of the obtained data allows to draw a conclusion that the developed composition of the ceramic material on the basis of the three-component system $SrO–Al_2O_3–SiO_2$ is promising for creating a gradient radio-absorbing material.

Further researches are aimed at studying the dielectric characteristics of the developed material in a wide frequency range of radio waves.

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