SPECIFICS OF OBTAINING A VACUUM-TIGHT WEAKLY CONDUCTIVE CERAMICS BASED ON BARIUM ALUMINATE

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Barium aluminate ceramics with iron (III) oxide and lithium hydroxide additives was obtained by solid-phase synthesis. It has been established that high-temperature treatment in an oxidizing environment contributes to the production of vacuum-tight samples that meet the "absolutely impermeable" tightness criterion, while having a density of 3.75 g/cm^3, compressive strength of 597.1 MPa, and electrical conductivity ranging from $1.50 \cdot 10^{-7}$ to 1.05×10^{-4} S/cm (at 90 – 300°C).

Keywords: barium aluminate, vacuum-tight ceramics, lithium hydroxide, iron oxide, electrical conductivity.

INTRODUCTION

The intensive development of vacuum technology necessitates the creation of high-quality ceramic materials and products with reproducible new properties and improved conventional characteristics. When used as an element of a vacuum system in a particle accelerator for removing static charge from the internal chamber surfaces, such ceramics should meet a number of requirements [1, 2]. Specifically, it must possess sufficient mechanical strength, which is especially important when producing vacuum-tight connections between metal and ceramics; have good vacuum properties; be sufficiently conductive to eliminate the accumulation of static charges due to the emission of particles from the accelerator and their deposition on the chamber walls (otherwise, the resulting electrostatic fields can lead to deviation and scattering of the accelerated beam). The conductivity of the coating should be equal or greater than the minimum permissible value to prevent the induction of high eddy currents [3].

Due to the combination of high strength, thermal, and chemical stability, barium aluminates are one of the types of ceramic materials of interest. The most common method of synthesizing aluminates is solid-phase sintering of oxides, hydroxides, or carbonates, which is characterized by simplic-

ity and the absence of toxic reaction products [4]. The issue of producing electrically conductive ceramics based on barium aluminate can be resolved by partial isomorphic substitution of aluminum oxide with iron oxide [5, 6]. Electrical conductivity of such ceramics results from the presence of single-element ions with different valences and from electron hopping between these ions: $Fe^{2+} \rightleftarrows Fe^{3+} + e^-$ (electronic "hopping" mechanism of conductivity) [7]. Furthermore, the conductivity of ceramics can be increased by incorporating alkali metal ions into their composition. Such ions (especially Na^+ and Li^+) have high mobility, which increases with temperature (ionic mechanism of conductivity) [8].

Solid-phase reactions involving crystalline components are characterized by complex dependency on multiple factors. The most important ones include reactivity of the solid reagents and heat treatment conditions during synthesis. To enhance reactivity and intensify the chemical interaction processes, crystalline reagents are subjected to mechanical treatment using various grinding devices. The optimal heat treatment conditions are established based on the results of studying the physical and mechanical characteristics of the synthesized material [9 – 12].

Currently, two main approaches are commonly used to produce vacuum-tight ceramics, including high-temperature synthesis of ceramic materials with and without pressure (hot pressing method, such as isostatic hot pressing) [13]. This article presents the results of studying the effect of both heat treatment approaches on the physical and mechanical proper-

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ties of barium aluminate ceramics with the additions of iron (III) oxide and lithium hydroxide (as a source of Li+).

EXPERIMENTAL

The method for producing ceramic material includes the preparation of a powder composition used to produce a molding mixture, and subsequent formation of ceramic blanks, followed by drying and high-temperature treatment. Powder compositions were obtained by using barium oxides (BaO according to GOST 10203–78) and alumina (γ-Al_2O_3

according to TU 6-68-164–99) in combination with current-conducting additives. Iron (III) oxide (Fe_2O_3 according to TU 6-09-5346–87) and lithium hydroxide (LiOH according to TU 6-09-3767–84) were used as such additives. Oxide materials were mixed with and without the additives in an AGO-3 activator (manufactured by "Novits" JSC, Russia) in the amount of 60g. All powder compositions were obtained under the same conditions: 100 g of the material (mixture) intended for treatment were loaded into a drum along with grinding media (steel balls measuring 6 and 10 mm in diameter and weighing 1800 g), followed by performing mechani-
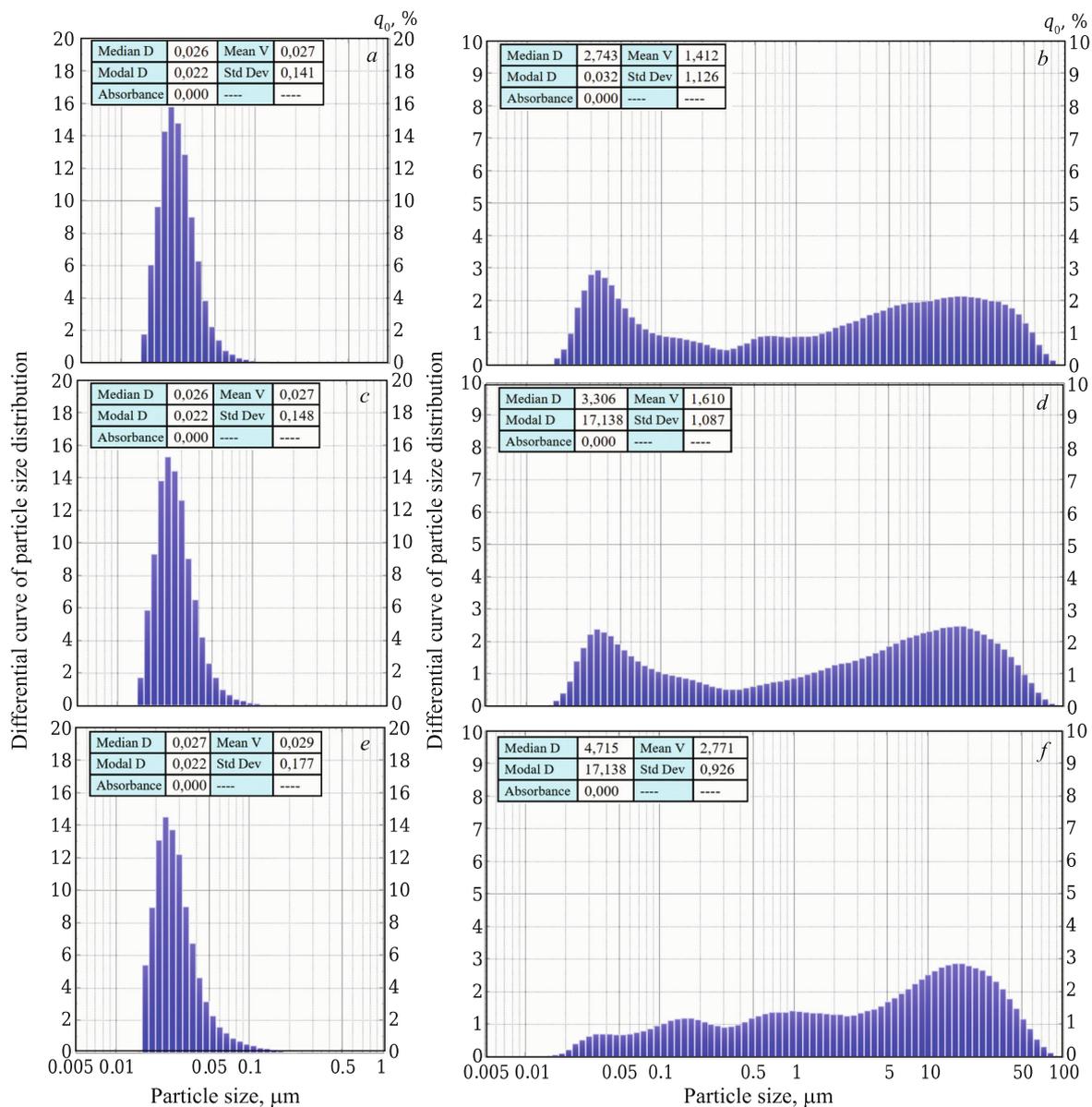

Fig. 1. Histograms of volumetric (*a, c, e*) and counting (*b, d, f*) particle size distributions for powder mixtures of compositions 1 (*a, b*), 2 (*c, d*), and 3 (*e, f*): Median D — average size of 50 % of sampling particles; Modal D — a maximum on the differential curve showing which particle size in this distribution has the highest percentage; Mean V — average particle size; Std Dev — corresponding standard deviation; Absorbance — particle absorptivity.

TABLE 1. Powder mixture composition.

Composition	Component content, wt.%			
	$\gamma\text{-Al}_2\text{O}_3$	BaO	Fe_2O_3	LiOH
1	79.96	20.04	—	—
2	61.95	18.64	19.41	—
3	61.60	18.50	19.30	0.60

cal treatment for 60 sec. The compositions of the powder mixtures are shown in Table 1.

The volumetric and counting distributions of the powder mixture particles based on their sizes were determined using a particle size analyzer SALD-7500 (Shimadzu). The average particle size was calculated as shown in Fig. 1.

By analyzing the histograms, it becomes obvious that the particle size range is quite wide, measuring from 0.02 to 100 μm for powder mixtures of all three compositions. In this case, based on the counting distribution histograms, the average particle sizes are practically the same (0.027, 0.027, and 0.029 μm for compositions 1, 2, and 3, respectively). As can be seen from the volumetric distribution histograms, the average particle sizes are 1.412, 1.610, and 2.771 μm. Compositions 1 and 2 demonstrate a pronounced bimodal volumetric distribution, while composition 3 is characterized by a polymodal distribution.

The molding mixture was prepared by using powder compositions mixed with distilled water (moisture content of the molding mixture — 9%). The resulting mixture was placed into steel molds and compacted on a PLG-20 hydraulic press at 200 MPa. The samples were air-dried for 24 hours, followed by oven drying at 200°C. High-temperature treatment of the samples was conducted at 1600°C.

The effect of the process conditions (regimes) of one of the main stages of solid-phase synthesis (i.e., high-temperature treatment (firing)) on the mechanical properties of ceramic materials was studied. Regime 1: heating samples at a rate of 200°C/h, soaking at 1600°C for 2 hours, followed by cooling at a rate of 100°C/h (firing performed in an oxidative (atmospheric air) environment). Regime 2: preliminary firing of the samples at 1500°C in an inert gas atmosphere (heating at a rate of 200°C/h, soaking at 1500°C for 2 hours, and cooling at a rate of 200°C/h), followed by hot isostatic pressing (HIP). The HIP treatment was conducted in an inert gas atmosphere (argon) and included heating at a rate of 200°C/h to 1600°C, while simultaneously increasing the chamber pressure to 200 MPa, holding under the specified conditions for 2 hours, and cooling at a rate of 200°C/h while reducing pressure. Firing of the samples according to regime 1 was carried out in the resistance furnace (model TK.16-1750.1F), preliminary firing according to regime 2 — in the resistance vacuum furnace (model SNVE-1.7.3.1.7/20), and HIP treatment of the samples – in the hot isostatic press (model AIP6-30H).

For the resulting ceramic samples, the following physical and mechanical characteristics were determined: average density, compressive strength, electrical conductivity, vacuum tightness, presence of material defects (of discontinuity type), and Vickers hardness. Samples of composition 1 without conductive additives were used as reference samples.

To analyze the microstructure of the samples, x-ray diffraction (XRD) and scanning electron microscopy (SEM) methods were used. The XRD analysis was conducted using a D8 Discover diffractometer (Bruker), and the identification of the x-ray diffraction patterns was performed using the ICDD PDF-2 database. The microstructure images were obtained using a TM1000 microscope (Hitachi, Japan) and a 3400S microscope equipped with an Inca x-ray fluorescence analysis attachment (Oxford Instruments, UK), capable of analyzing the spatial distribution of the elements (mapped composition in the imaging area).

The vacuum tightness of the synthesized ceramics was determined by measuring a helium leak rate of the pellet-shaped samples (diameter — 2.5 cm, height — 0.6 cm) over a period of 30 min using an Adixen ASM310 leak detector. A non-destructive testing was performed on an Eresco 65 MF4 x-ray machine by employing radiographic methods. The hardness of the ceramics was assessed using an EMCO-TEST DuraScan 50 microhardness tester after preliminary preparation of the samples using KEMET grinding wheels (grain sizes — 251, 107, 76, and 15 μm) and polishing cloths (6, 3, and 1 μm along with corresponding Aguapol-P diamond suspensions).

RESULTS AND DISCUSSION

The results of SEM analysis of the ceramics have shown that the material morphology is noticeably dependent on the presence of additives and the high-temperature treatment conditions. The structure of the samples without conductive additives is shown in Fig. 2a, b. As can be seen, it is quite porous and is mainly represented by lamella crystals.

According to the results of the morphological studies of ceramic compositions 2 and 3 (Fig. 2c – f), firing in an oxidative environment (regime 1) produces structural formations without a clearly identifiable geometric shape, whereas firing in an inert gas environment produces hexagonal crystals of mainly prismatic shape.

As demonstrated by the obtained mapping data, only ceramic samples of composition 2, fired in air, exhibit a sufficiently uniform distribution of elements Ba, Fe, and Al (Fig. 3a), which serves as an indirect evidence of the monophasic nature of the obtained ceramics. All other samples, regardless of the selected firing regime, are characterized by the presence of areas with uneven distribution of elements (Fig. 3b).

Studies of the phase composition of the compacted samples (composition 1) in an oxidative environment (Table 2) revealed the formation of barium hexaaluminate ($\text{BaAl}_{12}\text{O}_{19}$).
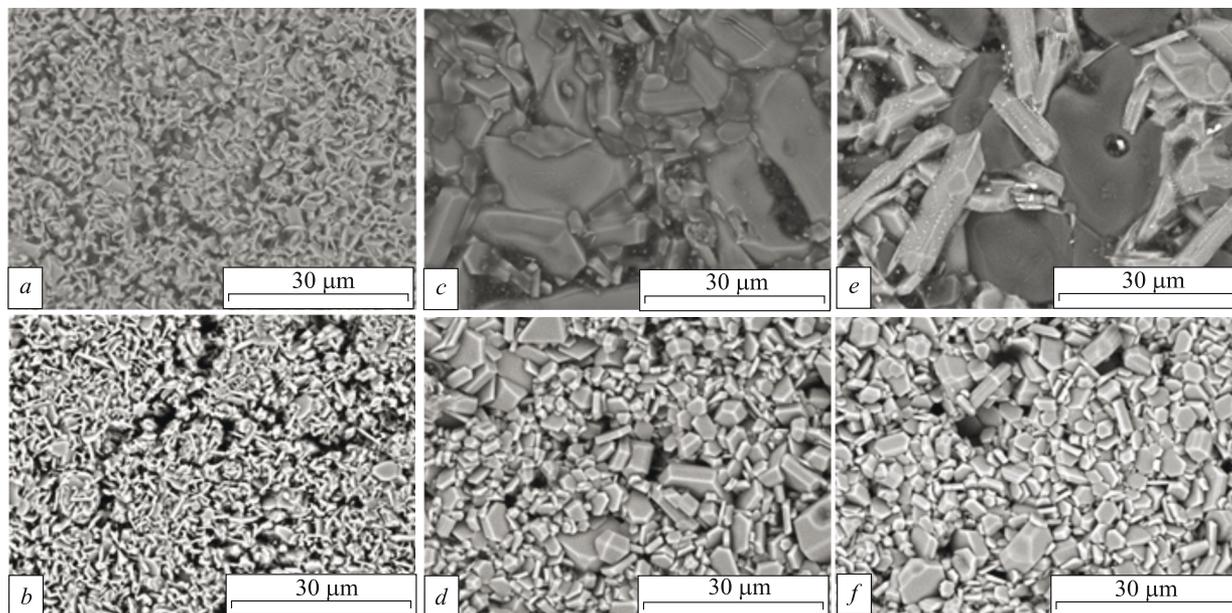
Fig. 2. SEM micrographs of the samples of compositions 1 (*a*, *b*), 2 (*c*, *d*), and 3 (*e*, *f*). Samples were produced according to regimes 1 (*a*, *c*, *e*) and 2 (*b*, *d*, *f*).
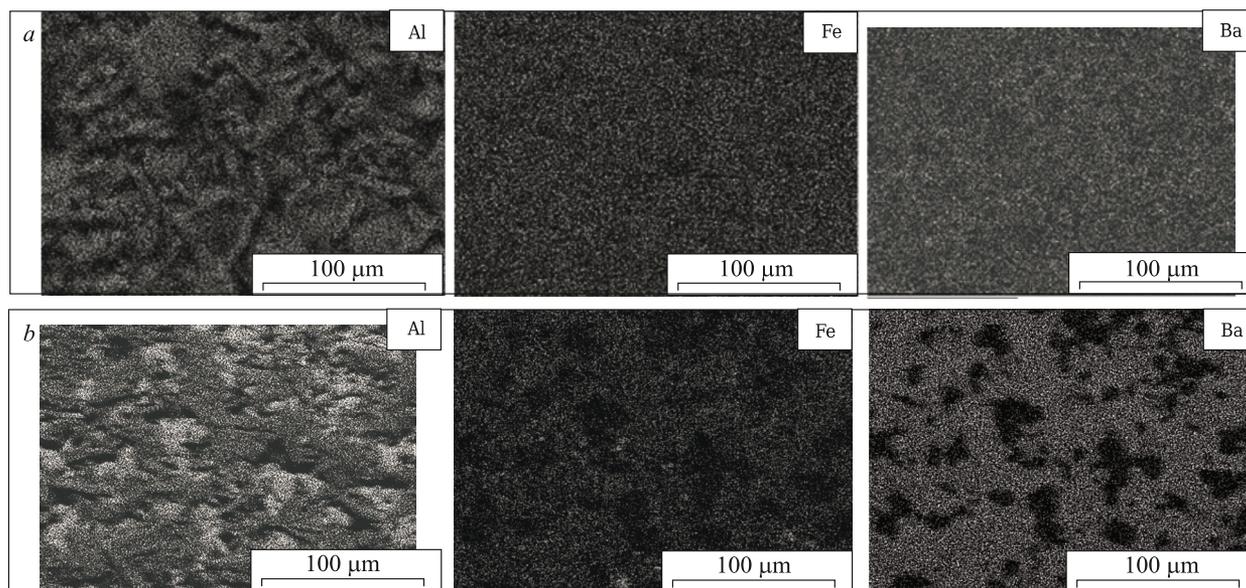

Fig. 3. Mapping data for ceramic samples of compositions 2 (*a*) and 3 (*b*) (regime 1).

Heat treatment in an inert gas atmosphere leads to the formation of a non-stoichiometric aluminate ($Ba_{0.956}Al_{11}O_{17}$) in addition to $BaAl_{12}O_{19}$. Essentially, the two hexaaluminate structures ($BaAl_{12}O_{19}$ and $Ba_{0.956}Al_{11}O_{17}$) are consistent with a slight difference in element concentration.

The introduction of an iron (III) oxide additive (composition 2) followed by firing in an oxidative environment leads to the formation of monophasic ceramics (iron-substituted barium aluminate — $Ba_2Fe_{11}Al_{11}O_{34}$), which is consistent

with the conclusion about a monophasity based on the mapping data. Alternatively, firing in an inert gas atmosphere produces biphasic ceramics ($Ba_2Fe_{11}Al_{11}O_{34}$ and $Ba_{0.956}Al_{11}O_{17}$).

When firing samples of composition 3 in both inert and oxidative environments, biphasic ceramics consisting of $Ba_2Fe_{11}Al_{11}O_{34}$ and $Ba_{0.956}Al_{11}O_{17}$ is produced.

Based on the analysis of physical and mechanical characteristics (Table 3), it has been established that the introduction of an iron (III) oxide additive (composition 2) provides

TABLE 2. Crystallographic phases of ceramic samples based on the XRD analysis.

Powder mixture composition	Crystallographic phase after firing	
	Regime 1	Regime 2
1	$BaAl_{12}O_{19}$	$Ba_{0.95}6Al_{11}O_{17}$, $BaAl_{12}O_{19}$
2	$Ba_2Fe_{11}Al_{11}O_{34}$	$Ba_2Fe_{11}Al_{11}O_{34}$, $Ba_{0.95}6Al_{11}O_{17}$
3	$Ba_2Fe_{11}Al_{11}O_{34}$, $Ba_{0.956}Al_{11}O_{17}$	$Ba_2Fe_{11}Al_{11}O_{34}$, $Ba_{0.95}6Al_{11}O_{17}$

TABLE 3. Properties of the structural ceramic samples produced according to regimes 1 and 2.

Powder mixture composition	Density, g/cm^3	Compressive strength, MPa	Hardness $HV20$
1	2.40/2.15	180.8/102.5	$P*$
2	3.67/3.39	542.7/485.0	721/489
3	3.75/3.31	597.1 /520.8	915/430

* P — insufficient sample strength for measuring hardness at this load.

an increase in density and strength of the ceramic samples, fired in an oxidative environment, by 52.9 and 201.5%, respectively, while the introduction of a mixed additive based on Fe_2O_3 and LiOH (composition 3) provides an increase by 56.3 and 230%, respectively. The maximum hardness of 915 $HV20$ was observed in samples obtained from the mixture of composition 3.

All ceramic samples, obtained using HIP treatment, have lower density and, hence, lower compressive strength com-

TABLE 4. Vacuum testing protocol*.

Powder mixture composition	Firing regime	Testing duration, min	Inleakage (helium leak rate), mbar·L/sec	Tightness criterion
2	2	5	3×10^{-7}	Gas-tight
3	2	30	$<5 \times 10^{-10}$	Absolutely vacuum-tight
2	3	1	2×10^{-2}	Water-tight
3	3	1	2×10^{-2}	Water-tight

* Pressure and tightness criterion are the same for all samples, constituting $1.5 \times 10^{-6} - 2.5 \times 10^{-6}$ mbar and 1×10^{-9} mbar·L/sec, respectively.

pared to the samples obtained by firing in an oxidative environment.

The vacuum tightness of the ceramic samples of compositions 2 and 3 was determined based on the helium leak rate. The obtained data are shown in Table 4. According to the data, the samples that demonstrate vacuum tightness (according to the "absolutely impermeable" tightness criterion [14]) are those of composition 3, which were fired in an oxidizing atmosphere. The respective helium leak rate was less than 5×10^{-10} mbar·L/sec. Ceramic samples of composition 2, fired in an oxidizing atmosphere, meet the "gas-impermeable" criterion, while all other samples do not meet the requirements for vacuum-tight materials.

The non-destructive testing of the vacuum-tight ceramic sample (Fig. 4b), conducted by a radiographic method, revealed no inhomogeneities and/or defects. For comparison, an image showing the results of the non-destructive testing of the reference sample is shown in Fig. 4a. The cracks and pores, seen on the images, are shown in dark color, while densifications — in light color.
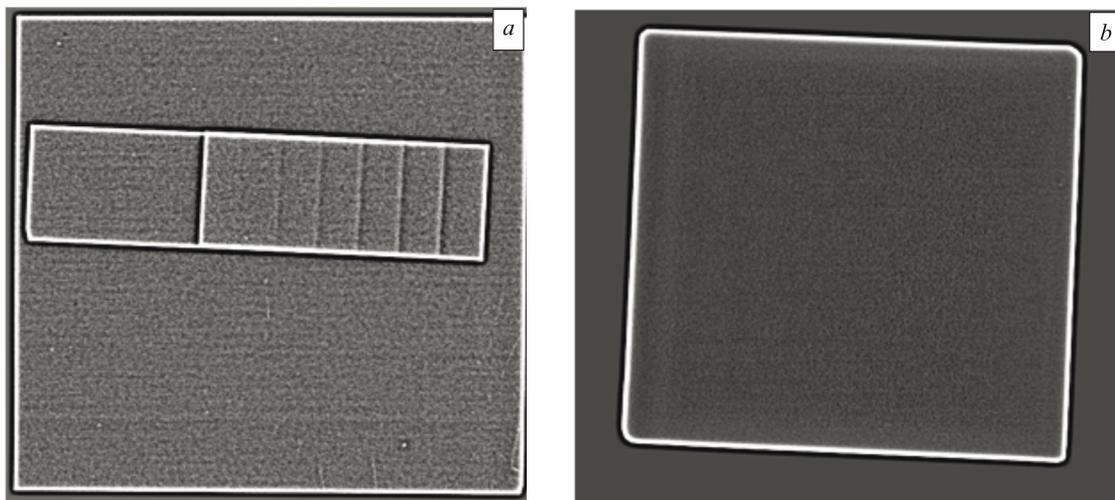
Fig. 4. Noon-destructive testing results for the reference sample (a) and ceramic sample of composition 3 (b).
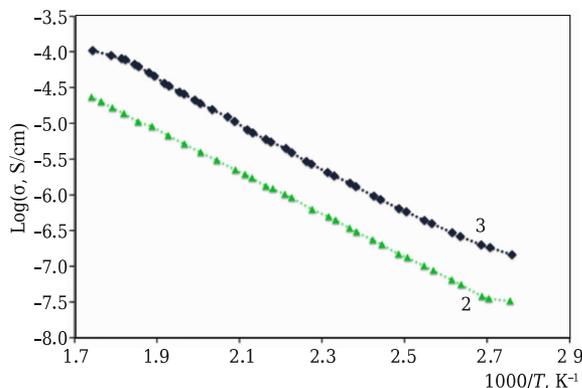
Fig. 5. Temperature dependence of electrical conductivity (σ) of ceramic samples of compositions 2 and 3 fired in an oxidizing environment.

Barium aluminate ceramics is a dielectric material [15]. By introducing iron (III) oxide and lithium hydroxide additives, it becomes possible to obtain electrically conductive ceramics. Analysis of the obtained data (Fig. 5) has shown that the conductivity of the samples strongly depends on temperature, varying from 3.09×10^{-8} to 2.14×10^{-5} S/cm (composition 2) and from 1.50×10^{-7} to 1.05×10^{-4} S/cm (composition 3) in the temperature range from 90 to 300°C.

Thus, samples of composition 3, fired in an oxidizing atmosphere, fully satisfy the requirements for ceramic materials used as elements of the vacuum system for removing static charge from the internal chamber surfaces by demonstrating vacuum tightness, electrical conductivity, and mechanical strength.

CONCLUSION

Ceramic materials based on barium and aluminum oxides with and without iron (III) oxide and lithium hydroxide additives were obtained by solid-phase synthesis using mechanical treatment during powder mixture preparation stage.

Dependence of the mechanical properties on the high-temperature treatment conditions has been demonstrated. By introducing a mixed Fe_2O_3 and LiOH additive into the powder mixture, followed by firing of the compacted sample in an oxidative environment, it becomes possible to obtain denser (by 56.3 %) and stronger (by 230 %) ceramic samples compared to those without additives. The corresponding helium leak rate is less than 5×10^{-10} mbar·L/sec, which satisfies the "absolutely impermeable" vacuum tightness criterion.

The introduction of Fe_2O_3 additive into the powder mixture makes it possible to obtain ceramic samples with electrical conductivity ranging from 3.09×10^{-8} to 2.14×10^{-5} S/cm

(at 90 – 300°C), while the addition of Fe_2O_3 and LiOH results in the electrical conductivity range of 1.50×10^{-7} to 1.05×10^{-4} S/cm.

REFERENCES

1. A. G. Vlasov, "Vacuum chambers and vacuum system of 15 – 25 MeV betatrons: circular electron accelerators," *Izv. Tomsk. Politekh. Inst.*, **87**, 301 – 306 (1957).
2. A. M. Levin, "Structural Materials and Sealants in Vacuum Equipment Manufacturing" [in Russian], Mashinostroyenie, Moscow (1986).
3. F. K. Goward, J. Lawson, J. Wilkin, and R. Carrathers, "The design of electron synchrotrons," *Journal of the Institution of Electrical Engineers*, **97**, 320 – 333 (1950).
4. M. Mohapatra, D. M. Pattanaik, S. Anand, and R. P. Das, "Effect of barium to aluminium ratio on phases leading to barium aluminates," *Ceram. Int.*, **33**, 531 – 535 (2007). DOI: 10.1016/j.ceramint.2005.10.019.
5. D. Naoufal, J. Millet, E. Garbowski, et al., "Synthesis, structure and catalytic properties of Fe-substituted barium hexaaluminates," *Catalysis Letters*, **54**(3), 141 – 148 (1998). DOI: 10.1023/A:1019004711495.
6. M. Machida, K. Equchi, and H. Arai, "High temperature catalytic combustion over cation-substituted barium hexaaluminates," Chemistry Letters, pages 767 – 770 (1987).
7. B. A. Belyaev, N. A. Drokin, and V. A. Poluboyarov, "Studying electrophysical characteristics of cation-substituted barium hexaaluminate ceramics by the impedance spectroscopy," *Fizika Tverdogo Tela*, **60**(2), 269 – 275 (2018). DOI: 10.21883/FTT.2018.02.45380.226.
8. V. L. Balkevich, Technical Ceramics: A Textbook for Technical Colleges [in Russian], Stroyizdat, Moscow (1984).
9. Yu. D. Tretyakov, Solid-phase Reactions [in Russian], Khimiya, Moscow (1982).
10. G. W. Brauer, Handbook of Inorganic Synthesis [in Russian], Mir, Moscow (1985).
11. A. West, Solid State Chemistry. Theory and Applications [in Russian], Mir, Moscow (1988).
12. E. I. Denisova, V. V. Kartashov, and V. N. Rychkov, Solid-phase Synthesis of Metal-oxide Powders: Study Guide [in Russian], GOU VPO UGTU-UPI, Yekaterinburg (2008).
13. R. A. Shutilova, V. L. Kuznetsov, S. I. Moseenkov, et al., "Vacuum-tight ceramic composite materials based on alumina modified with multi-walled carbon nanotubes," *Mater. Sci. Eng., B,* **254**, Article No. 114508 (2020). DOI: 10.1016/j.mseb.2020.114508.
14. Leybold, Book on Vacuum Technology: Fundamentals of Leak Detection [in Russian], translated by Leyficon Vacuum Service [Electronic resource], available at: https://leyficon.ru/pdf/osnovi-techeiskanie-leybold.pdf (access date: April 17, 2023).
15. M. E. Drits, P. B. Budberg, G. S. Burhanov, et al., Properties of Elements: A Reference Book [in Russian], ed. by M. E. Drits, Metallurgy, Moscow (1985).