# Investigation of the influence of temperature-time regimes on the morphological features of slawsonite ceramics

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## Abstract

The paper considers a new technology for obtaining ceramic materials based on slawsonite, which is a two-stage one. The first stage is the synthesis of the slawsonite phase and the grinding of the synthesized material. The second stage is the formation of raw material by the method of slip casting into plaster molds and the subsequent firing of the products. The effect of temperature-time regimes on the properties of slawsonite ceramics has been studied. Changeable technological parameters: firing temperature of products – 1,350 °C and 1,400 °C, exposure at maximum temperature – 2 and 4 hours. The morphology and phase features of the samples were studied by X-ray phase analysis and scanning electron microscopy. Regularities of changes in physical and mechanical properties depending on the temperature and duration of firing of experimental ceramics are established. It is proved that with an increase in the duration of firing of samples, the values of water absorption and open porosity decrease and the density of slawsonite ceramics increases. The mechanical and dielectric properties of experimental ceramics are experimentally studied, the values of which are in the ranges $\varepsilon$ = 5.8 - 13.2; $\sigma$ = 140 - 390 MPa.

Keywords: Slawsonite, radio-transparent materials, morphology, phase features, mechanical properties, dielectric properties
Kulcsszavak: Slawsonit, rádiótranszparens anyagok, morfológia, fázisjellemzők, mechanikai tulajdonságok, dielektromos tulajdonságok

## 1. Introduction

In wartime, the development of new types and classes of weapons is essential to ensure the state integrity of Ukraine. The development of new generations of guided air-to-air, air-to-surface missiles and anti-aircraft missiles requires the development and implementation of a wide range of materials with improved physicochemical, mechanical, thermal and electrophysical characteristics.

The interest of developers in the problem of creating radio-transparent ceramic materials with operating temperatures up to 1,500 °C is obvious. As a rule, materials for this purpose are powder ceramics based on refractory compounds. Powder technology in comparison with a sitall technology provides the increased stability and reproducibility of physical and chemical properties of materials. Modern technologies allow to obtain a wide range of properties through the manufacture of materials by modifying them with various additives to add special properties.

The relevance of the direction and research as a whole is in finding materials that can satisfy a set of specific requirements for the manufacture of aircraft elements and investigate the dependence of the influence of technological parameters on the structure that determines its properties.

## 2. Analysis of literature data and problem statement

Slawsonite ceramics is a fairly new and promising material for obtaining radio-transparent fairings. It belongs to electrical ceramics. Strontium anorthite $SrAl_2Si_2O_8$ belongs to the feldspar group of minerals, has a high melting point (1,765 °C), reduced thermal expansion coefficient ($6.5 \cdot 10^6$ 1/degree), low values of dielectric constant (6.0-7.0) and tangent. dielectric loss angle ($11.0 - 50.0 \cdot 10^{-4}$) in a wide temperature and frequency ranges [1-4]. The properties of slawsonite ceramics depend on the chemical and phase composition, macro- and microstructures, as well as on the technological methods of manufacturing products [5-7].

In the USA, to create more advanced high-temperature radio-transparent materials, glass-ceramics based on monoclinic strontium and barium aluminosilicates are considered, which has the following characteristics: dielectric constant $\varepsilon = 6.55 - 7.0$; dielectric loss tangent $\tan \delta = (8 - 25) \cdot 10^{-4}$, for strontium-containing compositions: $\varepsilon = 6.16 - 6.77$ and $\tan \delta = (11 - 50) \cdot 10^{-4}$ at 1,100 °C [8,9].

In works [10, 11], densely sintered materials based on strontium-anorthite ceramics with low temperature coefficient of linear expansion (TKLE) values (32.0 - 33.4) · $10^{-7}$ deg.$^{-1}$ were obtained, which causes their high heat resistance (not lower than 850 °C). High density values (2.40 - 2.50 g/cm$^3$) and mechanical compressive strength limits (237 - 246 MPa) are observed. In turn, the dense microstructure allows to achieve high dielectric values ($\varepsilon$ = 4.4 - 4.8; tgδ = 0.005 - 0.007) at a frequency of 10 GHz.

In South Korea, the solution to the problem of obtaining ceramic materials containing only the stable monoclinic form of slawsonite was achieved at Daejin University (Department of Materials Science and Engineering), which made it possible to obtain glass-ceramic composite materials with high radio transparency, strength, and low TKLE values. Glass ceramics containing monoclinic strontium anorthite were obtained based on the stoichiometric composition after crystallization at 1,100 °C for 1 hour or at a temperature of ≥ 1184 °C for a shorter period [12, 13].

However, the production of glass-ceramic materials based on aluminosilicate systems using network technology is an energy-intensive process (glass melting temperature is about 1,600 °C – 1,700 °C), and also introduces a limitation on the complexity of the forms of finished products. Therefore, it is important to take into account the availability and simplicity of the technology for obtaining the final product.

NTU "KhPI" performs works [14-16] on obtaining radio-transparent ceramics using ceramic technology by semi-dry pressing. The authors of the works investigated possible ways of formation and conditions of low-temperature synthesis of the slawsonite phase. In [16], slawsonite ceramics were obtained during single-stage firing in an induction laboratory furnace at a temperature of 1,550 °C with holding at this temperature for 5 hours. However, in this work, when forming samples, the semi-dry pressing method was used, which does not allow obtaining products of complex shape.

In modern conditions, in most areas of engineering and technology, they are most promising for use as structural products with an intergranular and uniform structure. All the most important properties of products are determined, as a rule, by the microstructure and phase composition of the material, which are determined by the structure of the initial powder, the firing mode, etc. Therefore, within the framework of this study, an important task is to develop technological parameters for creating a material that can meet a number of basic requirements for products obtained using slip casting.

## 3. The purpose and objectives of the study

The purpose of this work is to study the influence of technological parameters on the morphological features of slawsonite ceramics. To achieve these goals, it is necessary to solve the following tasks:

- to develop technological parameters for obtaining slawsonite radio-transparent ceramics by the method of water slip casting;
- to study the structural and phase features of the obtained ceramic samples;
- to study the operational and dielectric properties of the obtained samples, which determine the quality of finished products.

## 4. Materials and methods

Slawsonite was chosen as the main phase, which according to the level of electrophysical properties satisfies the requirements for radio-transparent materials and allows to obtain materials with a low reflection coefficient of radio waves and high heat resistance. G-00 alumina, strontium carbonate and quartz sand were used as raw materials, and a eutectic additive of lithium carbonate and stanum oxide was used to intensify the synthesis process.

Samples were prepared using a two-stage technology. In the laboratory, the mixture was homogenized by grinding raw materials in a ball mill with their subsequent passage through a sieve № 015. The resulting press powder was moistened with a solution of carboxymethyl cellulose («UGUR SELULOZ KIMYA», Turkey) moisture content - 8%. Then the formation of briquettes with dimensions of 50×20×50 mm from semi-dry masses was carried out by pressing the mixture on a manual hydraulic press MHP-10 under a pressure of 20 MPa. Drying in the oven was carried out at a temperature of 80 °C, to a residual humidity of not more than 1.0%. The synthesis in a muffle furnace at a rate of 10 degrees/min at a maximum firing temperature of 1250 °C with a holding time of 2 hours was performed. The synthesis of the synthesized substance took place for 10 minutes in the planetary mill Retch, before passing through a sieve № 0063 and the residue on it no more than 1.0%.

The slurry from the synthesized substance with a moisture content of 30% was obtained in a ball mill at a ratio of substance: ceramic layers 1:3, with the addition of a diluent Dolapix PC 67. To obtain the raw product a ready slurry was poured into gypsum mold. Drying of the raw material was carried out in an oven to a residual moisture of not more than 1.0%. The firing of the dried raw material was carried out in a silitic furnace Nabertherm in an accelerated mode: the rate of temperature accumulation – 12 - 15 degrees/min, the maximum firing temperature was 1350 °C and 1400 °C; exposure at maximum temperature – 2 and 4 hours. The fired products were subjected to machining.

Determination of dielectric properties was carried out on the immittance meter E 7 – 8 at a frequency of 1 kHz. Samples with a diameter of 37 mm and a thickness of 5 mm and an electrode diameter of 30 mm were used to determine the dielectric constant. To ensure a tight fit of the electrodes, the samples for research were ground. With the measured values of the electrical capacity of the samples, dielectric permeability was determined.

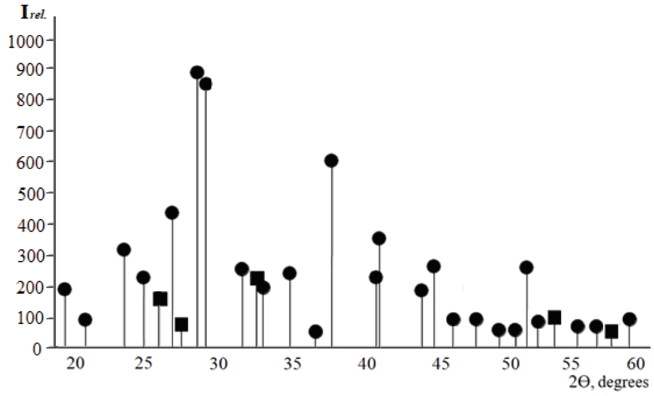
Determination of the apparent density and water absorption of the samples was carried out in a method of hydrostatic weighing in water.

The phase composition of the experimental samples was determined using the method of X-ray phase analysis (XRD). X-ray diffractograms were taken on a Dron-3M diffractometer with CuK$_\alpha$ – by radiation and a nickel filter under constant conditions of its operation.

The study of the microstructure of the samples and the morphology of the surface of their faults was carried out by direct scanning electron microscopy using a scanning electron microscope PhenomPro Desktop SEM (Thermo Fisher Scientific, USA) with an accelerating voltage of 15 kV.

## 5. Results and discussion

Ceramics synthesized at a temperature of 1250 °C with a holding time of 2 hours were investigated by X-ray phase analysis to determine the completeness of the reaction of formation of the slawsonite phase. The results of X-ray phase analysis are shown in *Fig. 1*.



*● – slawsonite ($SrAl_2Si_2O_8$), ■ – strontium metasilicate ($SrSiO_3$)*

*Fig. 1 Bar radiograph of slawsonite synthesized at a temperature of 1250 °C*
*1. ábra 1250 °C hőmérsékleten szintetizált slawsonit röntgenfelvétele*

At the synthesis temperature of 1250 °C (*Fig. 1.*) the data indicate that the reaction of slawsonite synthesis is not complete. In addition, to the peaks of the crystalline phase of slawsonite, insignificant peaks of the intermediate compound strontium metasilicate are observed. However, there are no peaks of carbonates, which indicates the complete course of the dissociation reaction of the compound $SrCO_3$. Due to this reaction, the synthesis of the phase is accompanied by a large fire shrinkage (up to 20%) and can lead to defects during firing of products by one-stage technology. In connection with the above, this research uses a two-stage ceramic technology for antenna fairings.

To conduct experiments to establish the best technological parameters for the production of fairings from slawsonite ceramics in the framework of this work, firing temperature of samples – 1350 °C and 1400 °C, and exposure time at maximum firing temperature – 2 and 4 hours were selected as the variable technological parameters. To compare the samples, their physical-mechanical and dielectric properties were studied. The result was the arithmetic mean of three parallel tests. The results of studies of samples of slawsonite ceramics are shown in *Table 1*.

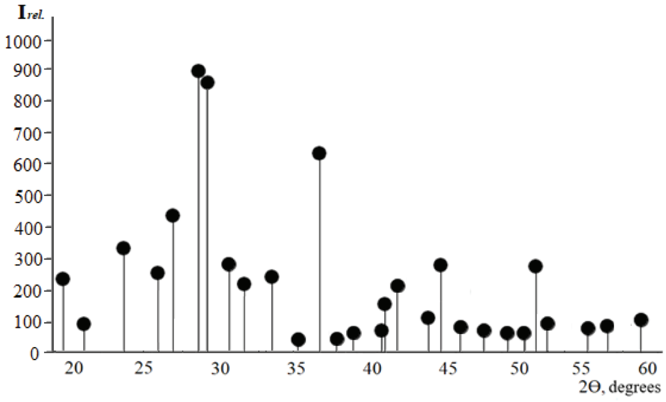
The fired samples were characterized by the absence of visible defects. From the obtained data we could see that with increasing the firing time from 2 to 4 hours, the indicators of both physical-mechanical and dielectric properties of slawsonite ceramics improve.

| $T_{firing}$, °C | τ $_{firing}$, hours | Water absorption, % | Open porosity, % | Apparent density, g/cm³ | Bending strength, MPa | Apparent dielectric permittivity |
|---|---|---|---|---|---|---|
| **1350** | 2 | 5.2 | 13.1 | 2.52 | 139 | 13.2 |
| | 4 | 0.3 | 0.7 | 2.85 | 392 | 5.8 |
| **1400** | 2 | 5.1 | 12.9 | 2.53 | 175 | 11.6 |
| | 4 | 4.2 | 10.8 | 2.60 | 219 | 9.7 |

*Table 1. Physical-mechanical and dielectric properties of samples of slawsonite ceramics*
*1. táblázat A slawsonit kerámiaminták fizikai-mechanikai és dielektromos tulajdonságai*

The best indicators of physical and mechanical properties of the test samples are obtained at a firing temperature of 1350 °C and exposure for 4 hours (water absorption – 0.3%, apparent density – 2.85 g/cm³, porosity – 0.7%, flexural strength – 392 MPa), which indicates a high density of the cast workpiece. The samples were also characterized by low apparent dielectric permittivity ε – 5.8, which meets the requirements for radio-transparent materials. The indicators of the investigated properties are close in values to the indicators of the samples of slawsonite ceramics obtained by the method of semi-dry pressing under the same conditions of the firing temperature – 1350 °C.

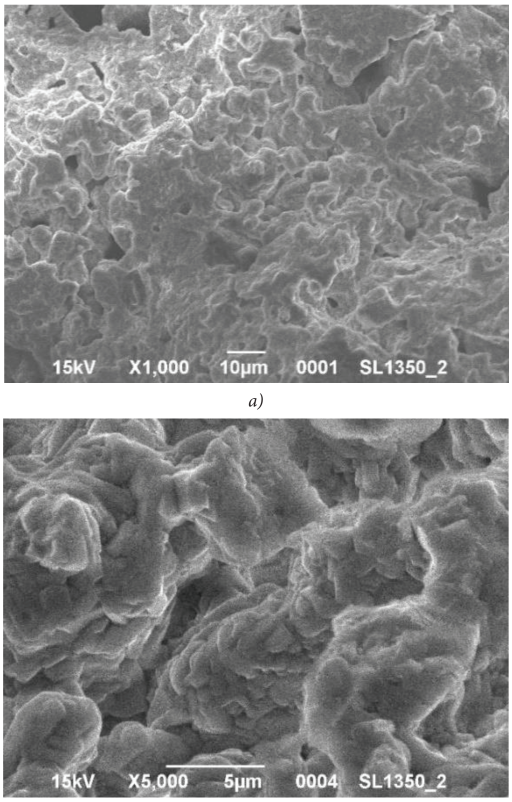
Structural and phase features of the obtained ceramics were studied by X-ray diffraction and scanning electron microscopy. The results of qualitative X-ray phase analysis showed that at firing temperatures above 1350 °C in all samples there is only the phase $SrAl_2Si_2O_8$, which indicates the completeness of the reactions of formation of the main phase. For example, *Fig. 2.* shows a bar-radiograph of samples obtained at a firing temperature of 1350 °C.



*● – slawsonite ($SrAl_2Si_2O_8$)*

*Fig. 2 Bar radiograph of slawsonite ceramics obtained at firing temperature of 1350 °C*
*2. ábra 1350 °C-os égetési hőmérsékleten készült slawsonite kerámiák röntgenfelvétele*

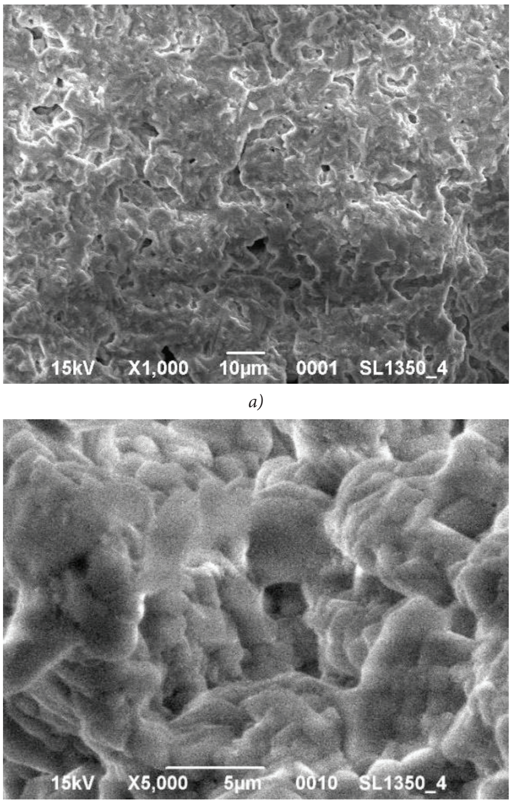
Morphological features of the surfaces of the obtained slawsonite ceramics were investigated using scanning electron microscopy. Photomicrographs of fractures of samples fired at temperatures of 1350 °C and 1400 °C and with exposure for 2 and 4 hours are shown in *Fig. 3-6.*



*b)*

*Fig. 3 Microstructure of samples of slawsonite ceramics at a holding time of 2 hours at a temperature of 1350 °C*

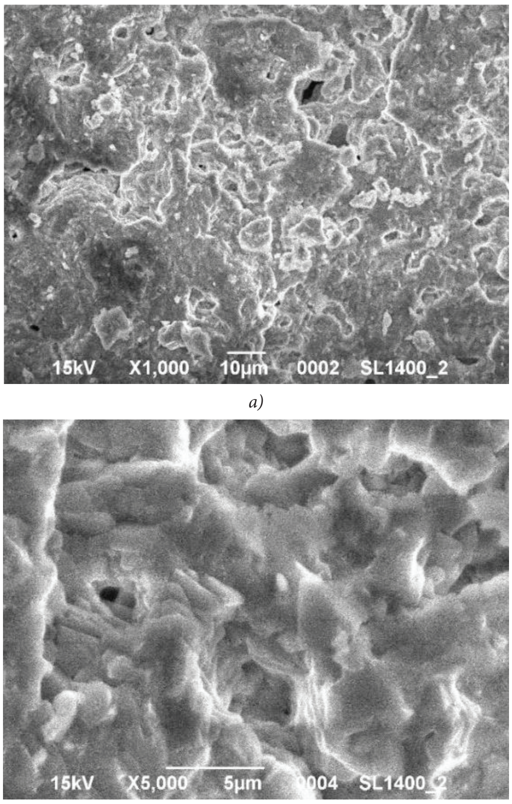
*3. ábra Az 2 óra hőtartással 1350 °C hőmérsékleten készített slawsonit kerámiaminták mikroszerkezete*



*b)*

*Fig. 4 Microstructure of samples of slawsonite ceramics at a holding time of 4 hours at a temperature of 1350 °C*

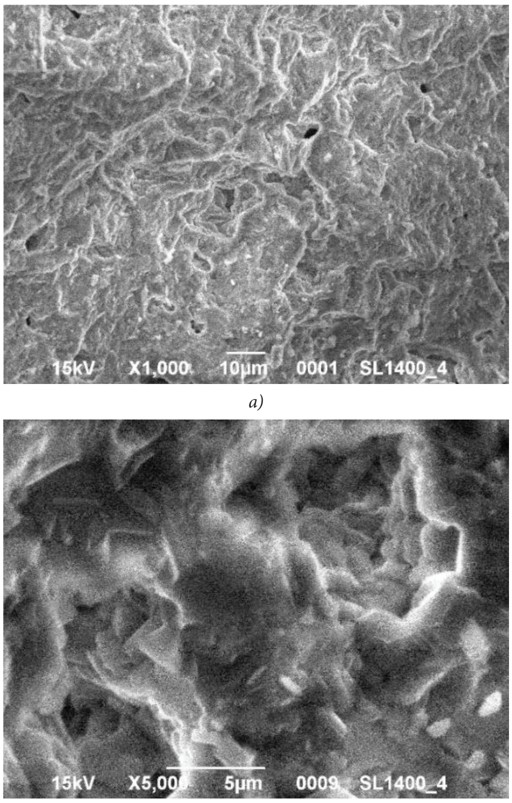
*4. ábra Az 4 óra hőtartással 1350 °C hőmérsékleten készített slawsonit kerámiaminták mikroszerkezete*



*b)*

*Fig. 5 Microstructure of samples of slawsonite ceramics at a holding time of 2 hours at a temperature of 1400 °C*

*5. ábra Az 2 óra hőtartással 1400 °C hőmérsékleten készített slawsonit kerámiaminták mikroszerkezete*



*b)*

*Fig. 6 Microstructure of samples of slawsonite ceramics at a holding time of 4 hours at a temperature of 1400 °C*

*6. ábra Az 4 óra hőtartással 1400 °C hőmérsékleten készített slawsonit kerámiaminták mikroszerkezete*

Images *Fig. 3 (a), 4 (a), 5 (a), 6 (a)* allow us to assess the natural roughness of the chip surface, the porosity of the samples and the homogeneity of the material structure. In the images *Fig. 3 (b), 4 (b), 5 (b), 6 (b)* starting from 1350 °C we could see the active growth of the crystalline structure of slawsonite.

In samples with a holding time of 2 hours at a firing temperature of 1350 °C, the presence of pores with a size of about 10 μm, which significantly impairs the mechanical properties of the samples. With increasing exposure time to 4 hours, we see a densely sintered, homogeneous structure with pores of no more than 1-2 μm and a clearer structure of slawsonite, which also reduces the dielectric permittivity. Based on the results of the study of the microstructure, we assumed that increasing the holding time to 4 hours has a positive effect on the operational and dielectric properties of the obtained ceramics.

According to the results of complex researches it is established that the material acquires the best properties at firing temperature of 1350 °C and endurance at maximum temperature for 4 hours in the studied area of technological parameters. Ceramic nose fairings obtained according to the recommended technological parameters of production have the following properties: water absorption – 0.7 - 0.9%, apparent density – 2.6 - 2.8 g/cm$^3$, porosity – 1.6 - 2.2%, limit bending strength – 340 - 360 MPa and apparent dielectric permittivity – 6.5 - 7.2.

The obtained materials based on slawsonite meet the requirements of the standard GOST 20419-83 (subgroup 420) and can be used for the creation of radio-transparent ceramics and the manufacture of radio-transparent ceramic nose fairings. It is established that according to the values of these characteristics, the materials belong to the radio-transparent ceramics and can be used in the aerospace industry for the manufacture of individual parts.

## 6. Conclusions

As a result of the work, the morphological features of slawsonite ceramics were investigated. The influence of technological parameters on the physical-mechanical and dielectric properties of the obtained ceramics is studied. According to the results of complex researches, the following technological parameters of production of radio-transparent ceramic nasal fairings on the basis of slawsonite are recommended: the first stage – synthesis at a temperature of 1250 °C, endurance time at the maximum temperature – 2 hours; the second stage is the formation of the fairing by the method of slip casting into gypsum molds, the firing temperature of the fairing – 1350 °C, the holding time at maximum temperature – 4 hours.

Ceramic nose fairings obtained by optimal technological parameters have the following properties: water absorption – 0.7 - 0.9%, apparent density – 2.6 - 2.8 g/cm$^3$, porosity – 1.6 - 2.2 %, strength bending – 340 - 360 MPa and apparent dielectric permittivity – 6.5 - 7.2.

Developed materials based on the slawsonite phase $SrAl_2Si_2O_8$ meet the requirements of GOST 20419-83 for technical ceramic products (subgroup 420-Celsius) and meet the requirements for modern radio-transparent ceramic materials.

### References

[1] Dear P.S. (1957) Phase in system SrO – $Al_2O_3$ – $SiO_2$. Bull. Virginia Polytechn. Inst. № 11. P. 50.

[2] Shukla A. (2012) Development of a critically evaluated thermodynamic database for the systems containing alkaline-earth oxides. Genie metallurgique. № 1. 349 p.

[3] Y.-M. Sung, S. Kim. (2000). Sintering and crystallization of off-stoichiometric SrO–$Al_2O_3$–$2SiO_2$ glasses. Journal of Materials Science, Vol. 35, pp. 4293–4299.

[4] C. Ferone, B. Liguori, A. Marocco, S. Anaclerio, M. Pansini, C. Colella. (2010). Monoclinic (Ba, Sr)-celsian by thermal treatment of (Ba, Sr)-exchanged zeolite A. Microporous and Mesoporous Materials, Vol. 134, pp. 65–71.

[5] Y. Kobayashi, M. Inagaki. (2004). Preparation of reactive Sr-celsian powders by solid-state reaction and their sintering. Journal of the European Ceramic Society, Vol. 24, pp. 399-404.

[6] A. Marocco, B. Liguori, G. Dell'Agli, M. Pansini. (2011). Sintering behavior of celsian based ceramics obtained from the thermal conversion of (Ba, Sr)-exchanged zeolite A. Journal of the European Ceramic Society, Vol. 31, pp. 1965–1973

[7] P. Ptáček, F. Šoukal, T. Opravil, E. Bartoníčková, J. Wasserbauer. (2016). The formation of feldspar strontian ($SrAl_2Si_2O_8$) via ceramic route: Reaction mechanism, kinetics and thermodynamics of the process. Ceramics International, Vol. 42, № 7, pp. 8170-8178.

[8] Pat. 7867932 US, MPK C 03 C 10/0036. Refractory glass ceramics / George H. Beall; zayavnik I patentovlasnik Corning Inc. № 11/895847 zayavl. 28.08.2007; opubl. 05.03.2009.

[9] Pat. 5642868 US, MPK C 04 V 35/195. Ceramic material / Inna G. Talmy, Deborah A. Haught; zayavnik I patentovlasnik US Secretary of Navy. № 518604 zayavl. 02.05.1990; opubl. 01.07.1997.

[10] O. Zaichuk, A. Amelina, Yu. Hordieiev, Y. Kalishenko, N. Sribniak, S. Halushka, D. Borodai, A. Borodai. (2020). Patternsin the synthesis processes, the microstructure and properties of strontium anorthite ceramics modified by glass of spodumene composition. Eastern-European Journal of Enterprise Technologies, Vol 6. № 6 (108). p. 15 – 26. DOI: https://doi.org/10.15587/1729-4061.2020.216754

[11] Andreev, M. V., Drobakhin, O. O., Privalov, Y. N., Saltykov, D. Y. (2014). Measurement of dielectric material properties using coupled biconical resonators. Telecommunications and Radio Engineering, 73 (11), 1017–1032. doi: https://doi.org/10.1615/telecomradeng.v73.i11.70

[12] Yun Mo Sung, Kwak Woo Chul. (2002) Influence of Various Heating Procedures on the Sintered Density of Sr-celsian Glass-ceramic. Journal of Materials Science Letters. Vol. 21, № 11, pp. 841–843. https://doi.org/10.1023/A:1015710309425

[13] Yun Mo Sung. (2000) Monocelsian formation in the SrO–$Al_2O_3$–$2SiO_2$ glass. Journal of Materials Science Letters. Vol. 19, pp. 453–454. https://doi.org/10.1023/A:1006724930508

[14] Lisachuk G.V., Kryvobok R.V., Zakharov A.V., Chefranov E.V., Lapuzina O.M., Voloshchuk V.V., Samoilenko N.N. (2019) Technological parameters of ceramics creation on the basis of slawsonite. Éptőanyag - Journal of Silicate Based and Composite Materials. Vol. 71, № 2. pp. 48-53. https://doi.org/10.14382/epitoanyag-jsbcm.2019.9

[15] Lisachuk G.V., Kryvobok R.V., Zakharov A.V. et al. (2017) Optimization of the compositions area of radiotransparent ceramic in the SrO – $Al_2O_3$ – $SiO_2$ system. Przeglad Elektrotechniczny. Vol. 92, № 3., pp. 79–82. doi:10.15199/48.2017.03.19

[16] Lisachuk G.V., Kryvobok R.V., Fedorenko E.Y., Zakharov A.V. (2015) Ceramic radiotransparent materials on the basis of BaO-$Al_2O_3$-$SiO_2$ and SrO-$Al_2O_3$-$SiO_2$ systems. Építőanyag – Journal of Silicate Based and Composite Materials. Vol. 67, № 1., pp.20–23. http://dx.doi.org/10.14382/epitoanyag-jsbcm.2015.4

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