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ENERGY-EFFICIENT SYNTHESIS OF ULTRA-DISPERSED POWDERS FOR OBTAINING RADIO-TRANSPARENT CERAMICS AND COMPOSITES

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The synthesis of refractory compounds requires special conditions and methods to ensure the effective conduct of the phase formation reactions to obtain target compounds. The main disadvantage of solid-phase synthesis of compounds that are of most significant interest for obtaining new functional ceramic materials is the high energy consumption due to high phase formation temperatures, the duration of the process, and the presence of impurities in raw materials that impair the properties of the synthesis products. It is the purity and reproducibility of the synthesis products, the high dispersion of the crystalline phase, and the uniformity of the grain size distribution that ensure not only the high strength of ceramics and composite materials for radio-engineering purposes, but also the necessary level of their functional properties, in particular, electrophysical properties. This work analyzes possible solutions to the problem of energy consumption in the synthesis of refractory compounds. The results of research aimed at the synthesis of compounds of the BaO(SrO, ZnO)$-$$Al_2O_3$$-$$SiO_2$ system, necessary for the manufacture of radio-transparent ceramic and composite materials using the technology of exothermic synthesis from mixtures containing barium and strontium nitrates, silica, and organic reducing agents, are discussed. The formulation and technological parameters for obtaining the target compounds and their combinations using the nitrate-citrate method have been developed. Ultra-dispersed powders of refractory compounds (celsian, slawsonite, and willemite), as well as their combinations (slawsonite+celsian, slawsonite+willemite, celsian+willemite, slawsonite+celsian+willemite), have been obtained under laboratory conditions. With the involvement of X-ray phase analysis and scanning electron microscopy, the structural and phase features of the reaction products have been studied, and the factors determining their purity and particle morphology of the obtained ceramic powders have been identified.

Keywords: radio-transparent, ceramic and composite materials, ultrafine powders, pyrosynthesis, nitrate-citrate method, phase composition, morphological features.

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Introduction

A necessary condition for obtaining radio-transparent ceramic and composite materials is the synthesis of target phases characterized by a set of required properties for producing high-temperature radio-transparent materials. These include a high melting point [1], the required level of dielectric characteristics ($\varepsilon<10$, $tg\delta<10^{-2}$) [2], as well as low density, low thermal conductivity, resistance to thermal shock, and chemical corrosion [1–3]. Aluminosilicates and silicates of alkaline-earth metals are typically used for this purpose, such as celsian ($BaAl_2Si_2O_8$), slawsonite ($SrAl_2Si_2O_8$), cordierite ($Mg_2Al_4Si_5O_{18}$), willemite (Zn_2SiO_4), spodumene ($LiAlSi_2O_6$), and others. The key requirement in selecting target phases is the preservation of structural stability and the electrophysical properties of the compound at elevated service temperatures, which determines the consistency of the electrophysical characteristics of the material as a whole [4].

The production of high-temperature radio-transparent ceramics requires special conditions and methods to ensure effective phase-formation reactions for obtaining compounds whose synthesis is necessary to provide the set of operational properties of the products. The main drawback of solid-phase synthesis of compounds of interest for novel functional ceramic materials is excessive energy consumption due to the high phase-formation temperatures [5], the long duration of the process, as well as the presence of impurities in the raw materials that deteriorate the properties of the synthesized products [6]. The purity and reproducibility of the synthesized products, high dispersity of the powders of target compounds, homogeneous grain size distribution, and the required phase composition are crucial for obtaining high-temperature radio-transparent ceramic and composite materials with high strength and thermal stability.

The above factors determine the high interest in mastering new methods for synthesizing refractory compounds, which can ensure the fulfillment of these requirements.

The aim of the research is the exothermic synthesis of ultrafine powders of celsian, slawsonite, and willemite (both separately and in combinations) using the nitrate–citrate method to minimize energy consumption at the synthesis stage of target compounds in the technology of radio-transparent ceramic and composite materials.

To achieve this aim, the following tasks were set:

– Analysis of possible solutions to the problem of high-energy consumption in the synthesis of refractory compounds;

– Development of a methodology for obtaining target compounds and their combinations using the nitrate-citrate method;

– Investigation of the phase composition and morphological features of the synthesized products.

Reducing the synthesis temperature of target compounds, as well as obtaining a high-purity product in the shortest possible time, remains a challenge that continues to attract the efforts of materials scientists [7–9]. Some progress has already been made in this direction. Still, no significant techno-economic effect has been achieved, which is explained by the peculiarities of celsian and slawsonite formation mechanisms.

It is known that celsian formation occurs through the slow transformation of metastable hexacelsian at high temperatures [10]. At the same time, hexacelsian can be synthesized by alternative, more energy-efficient methods: electrofusion [11], sol-gel [12], and ion exchange [13]. Thus, the key to developing energy-efficient BAS-ceramics and composites based on them is solving the problem of hexacelsian transformation into celsian.

In addition, the limitation in lowering the solid-phase synthesis temperature of slawsonite is the slow decomposition of strontianite ($SrCO_3$), which occurs in the temperature range of $875–1035^0$C due to the transformation of polymorphic modifications α-$SrCO_3 \rightarrow \beta$-$SrCO_3$, thereby inhibiting its phase-formation processes [14]. Moreover, the formation of undesirable intermediate strontium aluminates leads to gehlenite ($Sr_2Al_2SiO_7$), which decomposes into slawsonite at ~1600^0C, significantly increasing the energy consumption of its synthesis.

Over the past decade, many studies have aimed to reduce the synthesis temperatures of celsian and slawsonite using different approaches, such as employing semi-products as intermediate compounds [15], adding precursors [16] or mineralizer doping [11], forming solid solutions, or crystallizing glasses of stoichiometric composition [17], all of which contribute to some reduction in energy consumption.

Currently, attempts have been made to use methods alternative to conventional solid-phase high-temperature synthesis, such as high-energy mechanical-chemical activation, sol-gel synthesis, hydrothermal synthesis, chemical co-precipitation, RF magnetron sputtering, spray pyrolysis, microwave hydrothermal synthesis, ultrafast pyrosynthesis, etc. [18]. Literature data analysis indicates that alternative approaches to synthesizing refractory aluminosilicates and silicates are potentially economically efficient for producing technical ceramics with various functional applications, compared to conventional solid-phase synthesis. The advantages of such methods include reduced energy consumption, shorter processing cycles, and obtaining high-quality products with minimal impurities. However, most of these methods are not applied in industry due to the complexity of scaling up the technological process [19].

Considering the above, obtaining refractory compounds via exothermic synthesis is of interest. This process is based on chemical reactions accompanied by the release of a large amount of heat, sufficient to sustain the process without external heating. Owing to the heat released, the reaction can propagate spontaneously throughout the entire reaction mixture. One type of exothermic synthesis is pyrosynthesis, which can be used to obtain high-temperature compounds (borides, carbides, nitrides, and silicides of metals) that are valuable for high-tech industries in aerospace, energy, metalworking, and electronics, owing to the high thermal stability, hardness, and corrosion resistance of the resulting materials. However, the application's feasibility depends on the compound's composition and the thermodynamic conditions of its formation.

The main features of exothermic synthesis include:

– Energy efficiency (due to the absence of a need for large amounts of external energy);

– High reaction rate (typically synthesis occurs within seconds);

– Possibility of obtaining high-purity reaction products;

– Controllability of reactant ratios and process conditions, ensuring the production of materials with specified phase composition and properties.

At the same time, it should be considered that in synthesizing crystalline target phases, the reaction must provide sufficient heating for component diffusion and compound structure formation. To ensure self-propagation of the response and preservation of the stoichiometry of the synthesized compound, justified calculation of the exothermic mixture composition and accurate dosing of the components are critical. Otherwise, crystallization of intermediate phases (e.g., barium and strontium aluminates and silicates) may occur. Temperature control is also crucial, affecting the synthesized products' phase composition and determining their morphological features.

Thus, for celsian and slawsonite, as the main phases for obtaining high-temperature radio-transparent ceramics, pyrosynthesis is potentially feasible: the formation of target compounds is likely at relatively low temperatures (900–1050^{0}C) compared to conventional solid-phase synthesis (1350–1400^{0}C) [20]. However, the success of this approach depends on the availability of raw materials (pure technical products), the degree of exothermicity of the mixture, and temperature control to avoid the formation of secondary phases. In turn, the synthesis of willemite (Zn_2SiO_4) powder by pyrosynthesis is the simplest due to the high thermodynamic potential of the reaction. Willemite formation requires somewhat lower temperatures (1100–1200^{0}C), so in this case, exothermicity can be enhanced by using additional heat sources to ensure process stability and reproducibility of the product composition.

One of the promising approaches to implementing pyrosynthesis is the nitrate–citrate method, which enables the formation of target compounds through the creation of a homogeneous precursor mixture using water-soluble nitrates and organic compounds, particularly citrates, which act as a reducing agent and chelating agent. The method involves preparing aqueous solutions of metal nitrates with the addition of citric acid, which, as a complexing agent, stabilizes metal ions in solution and promotes the formation of a homogeneous mixture. Heating of the exothermic mixtures is accompanied by a rapid temperature rise and release of significant amounts of energy, leading to self-ignition of the mixture. This method ensures uniform distribution of elements in the mix at the molecular level, guaranteeing high purity of the synthesized products [21]. Furthermore, the method allows control over the size of crystalline structures by varying the temperature conditions of synthesis. Its implementation does not require specialized equipment; phase-formation processes occur in an air atmosphere.

Experimental

For the implementation of exothermic synthesis of target phases $BaAl_2Si_2O_8$ (C), $SrAl_2Si_2O_8$ (S), Zn_2SiO_4 (W), and their combinations (SC, SW, CW, SCW), the following chemically pure technical products were used: nitrates $Al(NO_3)_3$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2{\cdot}6H_2O$, as well as amorphous highly dispersed silicon dioxide (Oresil 300). Distilled water was used to prepare precursor solutions. Citric acid ($C_6H_8O_7$) and urea $(NH_2)_2CO$ were applied as reducing agents.

The nitrate-citrate pyrosynthesis was carried out according to the following procedure:

1. Preparation of precursor solutions considering the stoichiometry of the target compounds;
2. Preparation of the exothermic mixture from the precursor solutions at the specified ratio of the target compounds;
3. Introduction of technological additives into the exothermic mixture: citric acid (to prevent cation precipitation through the formation of citrate complexes) and ammonium nitrate NH_4NO_3 (to stabilize the solution);
4. Heating of the exothermic mixture until the onset of self-ignition;
5. Slow cooling of the reaction product to avoid the formation of secondary phases;
6. Calcination of the reaction product at 950^{0}C to complete the phase-formation reactions.

During the heat treatment in the nitrate-citrate synthesis of the target compounds, a complex set of reactions occurs, the main ones being:

– decomposition of nitrates with the release of oxides and gaseous products:

$Ba(NO_3)_2 \rightarrow BaO+2NO_2+12O_2$;

$Sr(NO_3)_2 \rightarrow SrO+2NO_2+12O_2$;

$Al(NO_3)_3 \rightarrow Al_2O_3+3NO_2+32O_2$;

– combustion of the organic matrix (citric acid, $C_6H_8O_7$), accompanied by the release of gaseous products:

$C_6H_8O_7+72O_2 \rightarrow 6CO_2+4H_2O$;

– formation of target compounds from phase-forming oxides:

$BaO+Al_2O_3+2SiO_2 \rightarrow BaAl_2Si_2O_8$;

$SrO+Al_2O_3+2SiO_2 \rightarrow SrAl_2Si_2O_8$;

$2ZnO+SiO_2 \rightarrow Zn_2SiO_4$.

Generalized phase-formation reactions during pyrosynthesis of target compounds are as follows:

$$Ba(NO_3)_2+2Al(NO_3)_3+2SiO_2+C_6H_8O_7 \rightarrow$$
$$\rightarrow BaAl_2Si_2O_8+H_2O+CO_2\uparrow+NO_2\uparrow+O_2\uparrow;$$

$$Sr(NO_3)_2+2Al(NO_3)_3+2SiO_2+C_6H_8O_7 \rightarrow$$
$$\rightarrow SrAl_2Si_2O_8+H_2O+CO_2\uparrow+NO_2\uparrow+O_2\uparrow;$$

$$2Zn(NO_3)_2{\cdot}6H_2O+SiO_2+C_6H_8O_7 \rightarrow$$
$$\rightarrow Zn_2SiO_4+7H_2O+CO_2\uparrow+N_2\uparrow.$$

Based on the above reactions, considering the specified ratios of the target phases (Table 1), the compositions of the exothermic mixtures were calculated.

For the individual synthesis of target phases (mixtures labeled as C, S, and W), the amounts of reagents containing phase-forming components in the exothermic mixtures were calculated according to the stoichiometry of the corresponding compounds. For mixtures intended for the simultaneous synthesis of two phases (SC, SW, CW) and three phases (SCW), the required amounts of reagents were determined considering their ratios of 1:1 and 1:1:1, respectively.

Aqueous solutions of metal nitrates were prepared by dosing and stirring at 60–70°C for 30 minutes to ensure the complete dissolution of salts.

To form a stable citrate complex and ensure effective chelation, the molar ratio of citric acid to phase-forming cations was maintained at 2:1. Ammonium nitrate solution was used to stabilize the mixture, maintaining pH ≈6–7. The amount of NH_4NO_3 was calculated based on the content of phase-forming oxides, with a ratio of NH_4NO_3 to the sum of oxides of 1:1.

The ratio of reducing agent to oxidizer (φ) was defined as the actual «reductant:oxidant» ratio relative to the stoichiometric «reductant:oxidant» ratio. If $\varphi=1$, no additional oxygen is required for complete oxidation. Values of $\varphi>1$ or $\varphi<1$ correspond to excess or insufficient reductant, respectively. In the case of $\varphi>1$, an incomplete oxidation of the reductant leads to the formation of a reducing atmosphere, eliminating the need for its artificial creation. In this study, the

Table 1

Chemical composition of mixtures (recalculated with respect to oxides) by the specified phase composition of the synthesized products

Designation of mixtures	Target phase composition of synthesis products, %	Oxide content, mol.%				
		BaO	SrO	ZnO	Al_2O_3	SiO_2
C	$BaAl_2Si_2O_8$ 100	25.0	–	–	25.0	50.0
S	$SrAl_2Si_2O_8$ 100	–	25.0	–	25.0	50.0
W	$ZnSiO_4$ 100	–	–	73.0	–	27.0
SC	$BaAl_2Si_2O_8$ 50 $SrAl_2Si_2O_8$ 50	12.1	12.9	–	25.0	50.0
SW	$SrAl_2Si_2O_8$ 50 Zn_2SiO_4 50	–	10.1	39.7	10.1	40.1
CW	$BaAl_2Si_2O_8$ 50 Zn_2SiO_4 50	9.7	–	40.7	9.7	39.8
SCW	$BaAl_2Si_2O_8$ 40 $SrAl_2Si_2O_8$ 40 Zn_2SiO_4 20	8.8	9.4	18.3	18.1	45.4

ratio was kept constant at φ=1.25.

Since barium and strontium nitrates are thermally stable, their decomposition reactions to form phase-forming oxides require increased heat release. To meet this condition, citric acid ($C_6H_8O_7$) was used as a reductant with urea $(NH_2)_2CO$. Such a combination enhances the exothermic effect and accelerates the synthesis process. The brightness of the glow evaluated the intensity of the pyrolytic reaction during the self-ignition of the exothermic mixture. It was established that the most intense combustion, accompanied by open flame above the surface of the mix, was observed at a molar ratio of citric acid to urea of 1:1.

The exothermic mixtures consisting of precursor solutions, chelating agent (NH_4NO_3), and reductants ($C_6H_8O_7$+$(NH_2)_2CO$) were heated until the onset of self-ignition caused by energy release. The pyrosynthesis was accompanied by gradual removal of organic residues and gases, resulting in a homogeneous product, a nanostructured oxide precursor of the target phases. To avoid secondary phases, it was necessary to strictly maintain the specified ratios of reagents, including the composite reductant, whose qualitative and quantitative characteristics determine the temperature regime of synthesis.

The reaction products were calcined in a muffle furnace at 950^{0}C, 1000^{0}C, and 1050^{0}C to complete the directed phase-formation process and remove residual organics. This allowed assessment of the effect of calcination temperature on the particle morphology of the synthesized powders with the required phase composition.

The phase composition of the synthesis products was determined by qualitative X-ray diffraction (XRD) analysis using a DRON-3M diffractometer with CuK_a radiation. The crystallite size was estimated from the width of diffraction maxima in the XRD patterns of powders using the Scherrer equation [22]:

$$d = \frac{K \cdot \lambda}{\beta \cdot \cos\theta},$$

where d is the crystallite size; β is the full width at half maximum of the peak, rad or 2θ units; λ is the X-ray wavelength; θ is the diffraction angle; K is the Scherrer shape factor; and n is the number of interplanar spacing δ_{hkl}.

Microstructural and morphological features were analyzed using scanning electron microscopy (SEM).

Results and discussion

The stages of the synthesis process of the target compounds are illustrated in Fig. 1. Heating of the precursor solutions of the exothermic mixtures resulted in a gradual increase in viscosity (Fig. 1a) and foaming (Fig. 1b). This process was accompanied by a rapid rise in temperature and intense energy release, causing self-ignition of the mixture (Fig. 1c), with combustion accompanied by a bright glow (Fig. 1d). After cooling, the reaction products were obtained in the form of lightweight, highly porous agglomerates.

Using citric acid combined with urea as a reductant ensured complete transformation of the initial components of the experimental mixtures during the exothermic synthesis. As a result, highly porous reaction products were formed, containing aggregates of irregular shape composed of fine crystalline particles.

To complete the phase-formation process, increase crystallinity of the synthesized products, and remove organic impurities that may remain after pyrosynthesis, the obtained ceramic powders were subjected to heat treatment with 1-hour holding at

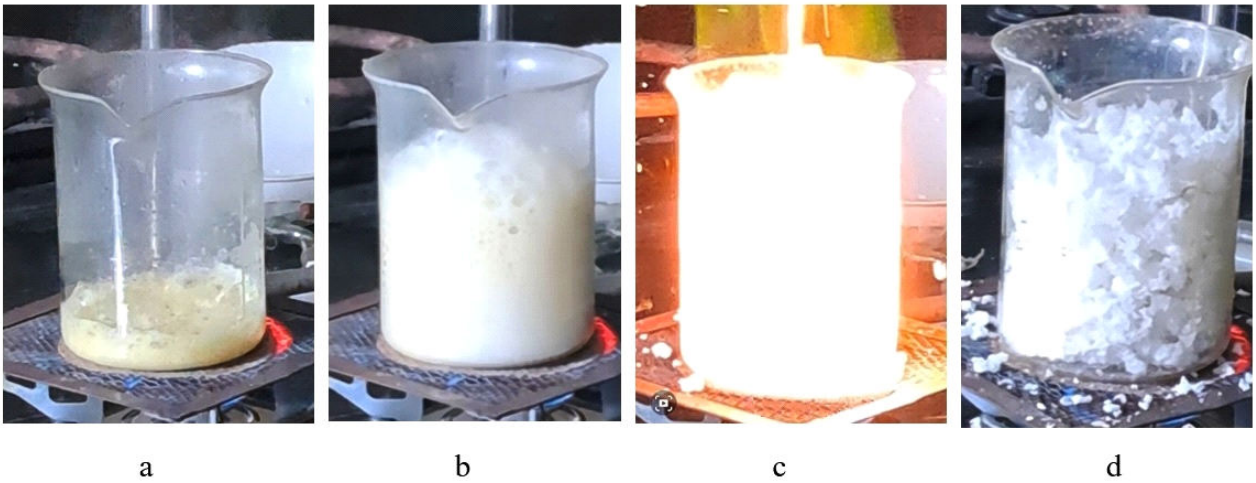

a b c d

Fig. 1. Stages of pyrosynthesis of the target compounds: a – gel formation; b – foaming; c – self-ignition and combustion of the exothermic mixture; d – cooling

950⁰C. This technological procedure, known as «calcination», allows obtaining synthesis products with a content of target phases of 96–98%. Figure 2 presents the appearance of synthesis products obtained using the CW mixture after cooling and calcination at 950⁰C for one hour.

The composition of the exothermic synthesis products was determined using X-ray diffraction (XRD) analysis. Figure 3 shows fragments of XRD patterns of the pyrosynthesis products before and after thermal treatment. As can be seen, the synthesis products obtained from the exothermic mixtures C, S, SC, and SW are predominantly X-ray amorphous. In turn, the XRD patterns of the CW and SCW mixtures reveal reflections of the target phases, though of low intensity, indicating the small size of crystalline formations.

Further heating and holding at 950⁰C complete the phase-formation reactions of thermodynamically stable phases and increase the crystallinity of the synthesis products. For example, only the corresponding target phases were identified in the synthesis products of the S, SW, and SCW mixtures subjected to 1 h thermal treatment at 950⁰C.

A solid solution of celsian and slawsonite was identified in the SC sample. Its formation is favorable due to the similar tectosilicate structure of these compounds and the close ionic radii of alkaline earth metals (Ba ≈0.149 nm, Sr ≈0.132 nm), which minimizes the energy cost of lattice deformation. In addition, Ba^{2+} and Sr^{2+} ions have the same charge, and thus do not disturb the electro-neutrality of the crystal when forming a solid solution via a substitution mechanism.

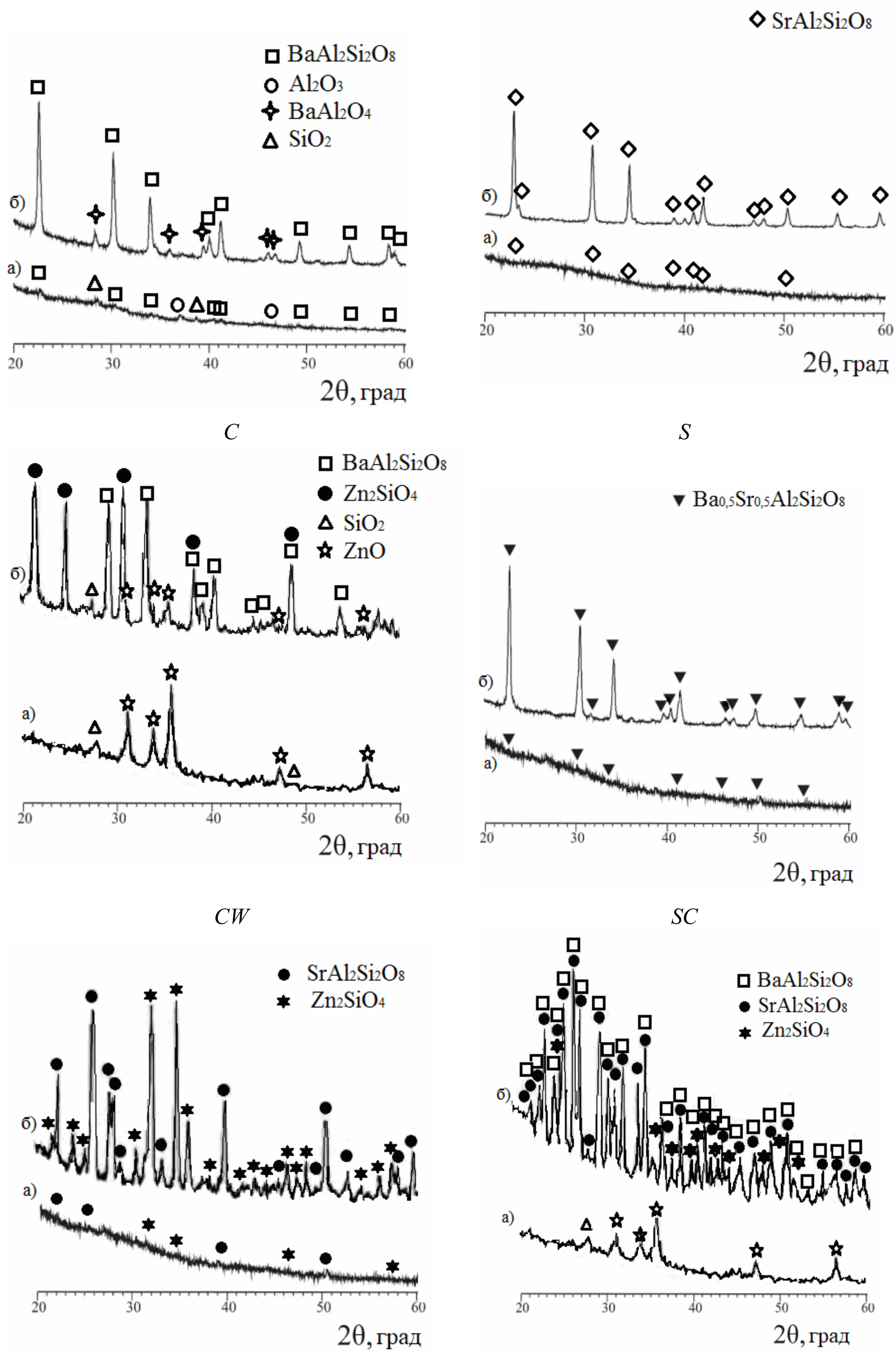
It should be noted that the ability of celsian and slawsonite to form solid solutions is a technological approach enabling directed adjustment of dielectric characteristics through variation of the Ba/Sr ratio. This improves microstructural homogeneity and material density, stabilizes thermal expansion, enhances resistance to abrupt temperature fluctuations, and increases mechanical strength due to reduced lattice stresses. Partial substitution of Ba with Sr in the crystalline lattice not only decreases dielectric losses of solid-solution-based materials with the general formula $Ba_xSr_{1-x}Al_2Si_2O_8$, but also promotes the formation of a more stable celsian structure at relatively low temperatures (≈1100⁰C), thereby reducing the risk of forming the undesirable hexacelsian structure. Due to its structural peculiarities, it is known that upon cooling, the hexacelsian phase induces significant volume changes (up to 2%), causing internal stresses and microcrack formation. Such behavior of ceramics based on celsian–slawsonite solid solutions is advantageous when fine-tuning materials for specific frequencies and operating conditions of radome applications in missiles and aircraft (e.g., aviation radar).

In turn, the CW mixture product contains residual phase-forming oxides (ZnO and SiO_2) that remain unreacted, identified in the material as zincite and quartz. Meanwhile, the C mixture product, apart from phase-forming oxides (Al_2O_3 and SiO_2), contains an intermediate phase, $BaAl_2O_4$. According to the $BaO-Al_2O_3-SiO_2$ phase diagram, this orthorhombic phase is stable up to 1600⁰C, and only under excess conditions transforms into $BaAl_2Si_2O_8$. However, this transition requires higher temperatures and longer durations. Typically, $BaAl_2O_4$ forms if the Al_2O_3/SiO_2 ratio >0.5. To prevent its formation, synthesis conditions should be adjusted: modify the molar ratio of phase-forming oxides for celsian synthesis toward an excess of SiO_2, ensure maximum homogenization of the mixture, and increase synthesis temperature and duration.

It is evident from Fig. 3 that the reflections of target phases in the XRD patterns of most samples have low intensity and a diffuse character. As is known


a
b

Fig. 2. Appearance of synthesis products (example of the CW mixture): a – after cooling; b – after calcination at 950⁰C



C *S*

CW *SC*

SW *SCW*

Fig. 3. XRD patterns of exothermic synthesis products of different compositions before and after the treatment at 950^{0}C

[1], broadening and low intensity of reflections are typical indicators of high dispersity of the crystalline phase. Considering the significant effect of particle size on sintering processes and the properties of radio-transparent ceramics, particle size evaluation of the obtained ceramic powders was further performed. Analysis of the XRD patterns allowed estimation of crystallite sizes in the synthesis products. Average particle size was calculated using the Scherrer method based on the width of diffraction maxima [22]. The calculations showed that crystallite sizes in the pyrosynthesis products obtained with the experimental exothermic mixtures ranged from 35 to 70 nm. It should be noted that the Scherer equation only estimates particle size, since it accounts for peak broadening related only to size effects, while neglecting the influence of internal lattice stresses.

SEM micrographs (Fig. 4) illustrate, at different magnifications, the morphological features of an ultra-dispersed powder of slawsonite+willemite composition obtained from the SC exothermic mixture.

The SEM images show that the synthesis products consist of porous agglomerates 2–12 μm, composed of delicate primary crystalline formations of irregular shape with dimensions up to 1 μm. Individual particles exhibit submicron sizes (≈300–500 nm). Increasing the calcination temperature of the synthesis products to 1000⁰C and above results in growth of the primary ceramic particles and their agglomeration, regardless of the synthesis products' composition.

Conclusions

1. Experimental studies demonstrated the feasibility of the nitrate-citrate pyrosynthesis method for obtaining target compounds that determine the ability of ceramic materials to transmit electromagnetic waves in the radio-frequency range. Using this method under laboratory conditions, ultra-dispersed powders of refractory compounds (celsian, slawsonite, and willemite) and their combinations (slawsonite+celsian, slawsonite+willemite, celsian+willemite, slawsonite+celsian+willemite) were synthesized. The nitrate-citrate method is flexible and can be adapted for synthesizing other refractory compounds and their mixtures.

2. It was shown that the phase composition of the obtained ceramic powders depends not only on the composition of the exothermic mixture but also on the temperature provided by a given exothermic reaction. Using citric acid as a reductant ensures complete transformation of the initial components of the exothermic mixtures and the formation of ultra-dispersed ceramic powders of the desired composition. Alternative reductants (urea or glycine) may adjust synthesis temperature, differing composition, chemical structure, and the amount of gaseous products released. The temperature and duration of thermal treatment mainly influence the particle morphology of ceramic powders. It was established that short-term heating at 950⁰C increases the crystallinity of the synthesis products, while treatment above 1000⁰C is undesirable due to the growth of primary crystalline particles.

3. The synthesized ultra-dispersed powders can produce ceramic and hybrid composite materials for radio-transparent protective structures of electronic devices operating in the microwave range. It can be expected that the high dispersity of pyrosynthesized ceramic powders will enable the formation of fine-grained microstructures in radio-transparent ceramics, thereby improving their functional and mechanical properties.

4. The results confirm the advantages of the illustrated synthesis method of ultra-dispersed refractory compounds regarding energy efficiency and economic feasibility. This approach allows the reduction of energy

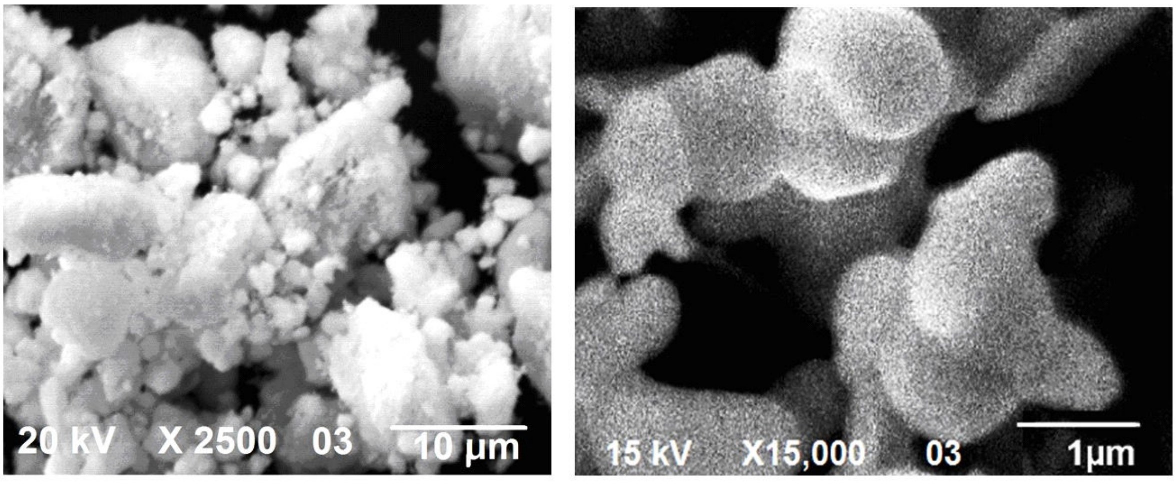


Fig. 4. SEM images of SC mixture synthesis products after thermal treatment of the powder at 950⁰C

costs for the synthesis of refractory compounds and shortens the production cycle of radio-transparent ceramic materials. Future research will focus on optimizing the pyrosynthesis parameters within the nitrate-citrate method and exploring scaling pathways for industrial production of radio-transparent ceramics.

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ЕНЕРГОЕФЕКТИВНИЙ СИНТЕЗ УЛЬТРАДИСПЕРСНОГО ПОРОШКУ ДЛЯ ОДЕРЖАННЯ РАДІОПРОЗОРОЇ КЕРАМІКИ ТА КОМПОЗИТІВ

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Синтез тугоплавких сполук вимагає спеціальних умов та методів для забезпечення ефективного проведення реакцій фазоутворення для одержання цільових сполук. Основним недоліком твердофазного синтезу сполук, що становлять найбільший інтерес для одержання нових функціональних керамічних матеріалів, є висока енергоємність через високі температури фазоутворення, тривалість процесу та наявність домішок у сировині, які погіршують властивості продуктів синтезу. Саме чистота та відтворюваність продуктів синтезу, висока дисперсність кристалічної фази та однорідність розподілу зерен за розмірами забезпечують не тільки високу міцність керамічних та композитних матеріалів радіотехнічного призначення, але й необхідний рівень їх функціональних властивостей, зокрема електрофізичних. У даній роботі проаналізовано можливі шляхи вирішення проблеми енергоспоживання при синтезі тугоплавких сполук. Обговорюються результати досліджень, спрямованих на синтез сполук системи BaO (SrO, ZnO)$-$Al$_2$O$_3$$-SiO_2$, необхідних для виготовлення радіопрозорих керамічних та композиційних матеріалів за технологією екзотермічного синтезу із сумішей, що містять нітрати барію та стронцію, кремнезем та органічні відновники. Розроблено рецептуру та технологічні параметри для одержання цільових сполук та їх комбінацій нітрат-цитратним методом. У лабораторних умовах отримано ультрадисперсні порошки тугоплавких сполук (цельзіану, славсоніту та віллеміту), а також їх комбінацій (славсоніт+цельзіан, славсоніт+віллеміт, цельзіан+віллеміт, славсоніт+цельзіан+віллеміт). За допомогою рентгенофазового аналізу та скануючої електронної мікроскопії досліджено структурні та фазові особливості продуктів реакції, а також визначено фактори, що визначають їх чистоту та морфологію частинок отриманих керамічних порошків.

Ключові слова: радіопрозорість, керамічні та композиційні матеріали, ультрадисперсні порошки, піросинтез, нітрат-цитратний метод, фазовий склад, морфологічні особливості.

ENERGY-EFFICIENT SYNTHESIS OF ULTRA-DISPERSED POWDERS FOR OBTAINING RADIO-TRANSPARENT CERAMICS AND COMPOSITES

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The synthesis of refractory compounds requires special conditions and methods to ensure the effective conduct of the phase formation reactions to obtain target compounds. The main disadvantage of solid-phase synthesis of compounds that are of most significant interest for obtaining new functional ceramic materials is the high energy consumption due to high phase formation temperatures, the duration of the process, and the presence of impurities in raw materials that impair the properties of the synthesis products. It is the purity and reproducibility of the synthesis products, the high dispersion of the crystalline phase, and the uniformity of the grain size distribution that ensure not only the high strength of ceramics and composite materials for radio-engineering purposes, but also the necessary level of their functional properties, in particular, electrophysical properties. This work analyzes possible solutions to the problem of energy consumption in the synthesis of refractory compounds. The results of research aimed at the synthesis of compounds of the BaO(SrO, ZnO)$-$Al$_2$O$_3$$-SiO_2$ system, necessary for the manufacture of radio-transparent ceramic and composite materials using the technology of exothermic synthesis from mixtures containing barium and strontium nitrates, silica, and organic reducing agents, are discussed. The formulation and technological parameters for obtaining the target compounds and their combinations using the nitrate-citrate method have been developed. Ultra-dispersed powders of refractory compounds (celsian, slawsonite, and willemite), as well as their combinations (slawsonite+celsian, slawsonite+willemite, celsian+willemite, slawsonite+celsian+willemite), have been obtained under laboratory conditions. With the involvement of X-ray phase analysis and scanning electron microscopy, the structural and phase features of the reaction products have been studied, and the factors determining their purity and particle morphology of the obtained ceramic powders have been identified.

Keywords: radio-transparent; ceramic and composite materials; ultrafine powders; pyrosynthesis; nitrate-citrate method; phase composition; morphological features.

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