

**SYNTHESIS AND PROPERTIES OF BISMUTH SILICATES PREPARED VIA
MECHANOCHEMICAL SYNTHESIS**

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**СИНТЕЗ И СВОЙСТВА СИЛИКАТОВ ВИСМУТА, ПРИГОТОВЛЕННЫХ МЕТОДОМ
МЕХАНИЧЕСКОЙ АКТИВАЦИИ**

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***Аннотация.** В настоящей работе были синтезированы серии силикатов висмута методом механической активации, а также исследованы их свойства такими методами, как ТГ-ДСК анализ и РФА-спектроскопия. Установлено, что для серии, приготовленной с соотношением реагентов $Bi:Si = 2:1$ после $800\text{ }^{\circ}\text{C}$ наступает плавление, тогда как для серии с эквимолярным соотношением Bi и Si в исходных реагентах плавления в этом температурном интервале не наблюдается. Показано, что при увеличении температуры прокаливания с $500\text{ }^{\circ}\text{C}$ до $700\text{ }^{\circ}\text{C}$ фаза метасиликата висмута (Bi_2SiO_5) полностью переходит в ортосиликат висмута ($Bi_4Si_3O_{12}$), а доля фазы силленита ($Bi_{12}Si_{20}$) увеличивается при увеличении соотношения $Bi:Si$.*

Introduction. Bismuth silicates are well-known compounds that have been recently drawing the interest of researchers due to their peculiar properties. Materials based on bismuth and silicon compounds appear to be potent for the usage in scintillators [1], gamma ray shields [2], and environmentally friendly lead-free ferroelectrics [3]. New methods for the preparation of such systems could increase the range of their application, as well as provide better alternatives in the existent research areas. The aims of the present research are a) to employ the mechanical activation technique in order to synthesize several series of bismuth silicates, b) to investigate their properties, and c) to define the influence of the starting BiSi atom ratio and calcination temperature on the resulting phase composition of the samples.

Materials and methods. Two series of bismuth silicates were prepared via mechanical mixing technique. The time of mixing = 3 min. The source of Bi was α - Bi_2O_3 prepared via calcination of $Bi(NO_3)_3 \cdot 5H_2O$ (Vekton, analytical grade) at $800\text{ }^{\circ}\text{C}$, while the source of Si was amorphous silica gel (Reakhim, analytical grade). The initial series of the samples was prepared with the atomic ratio of $Bi:Si = 1$, with BSM-1 being an uncalcined sample, while BSM-1a and BSM-1b being the samples calcined at $500\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$, respectively. The following series of the samples was synthesized with the atomic ratio of $Bi:Si = 2$, with BSM-2 being an uncalcined sample, while BSM-2a and BSM-2b being calcined at $500\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$, respectively.

The samples were studied via TG-DSC analysis (NETSCH Jupiter STA 449 F1 Thermal Analyzer) in the temperature range of 20 to 900 °C with the heating speed of 10°/min in the atmosphere of air. The phase composition of the samples was investigated on Shimadzu XRD-6000 diffractometer with the use of CuK α -radiation in the range of $2\theta = 5$ to 80 degrees with the measurement speed of 2°/min.

Results and discussion. The results of TG-DSC analysis are shown in Fig. 1. According to the presented data, uncalcined sample BSM-1 (Bi:Si = 1:1) does not demonstrate any notable endothermic peaks. The total weight loss of 2,41% is attributed to the water removal. The uncalcined sample BSM-2 (Bi:Si = 2:1), however, demonstrates a different behavior prior to heating – starting from 805°C where a phase transition can be observed. This endothermic peak is attributed to the sample melting, while the total weight loss of 1,48% is attributed to water evaporation.

The phase composition of the samples is given in Table 1. As shown, the uncalcined samples (BSM-1 and BSM-2) do not manifest any signs of formed bismuth silicate crystallites. However, a smaller part of the amorphous SiO₂ content is transformed to crystalline quartz (BSM-1, BSM-2) and coesite (BSM-2). The sample having an increased amount of bismuth (BSM-2) also indicates a variety of intermediate bismuth oxide phases different from α -Bi₂O₃. Despite the fact that all of the samples calcined at 500 °C (BSM-1a, BSM-2a) possess metastable Bi₂SiO₅ phase, it is completely transformed to the more stable bismuth orthosilicate Bi₄Si₃O₁₂ prior to the increase in calcination temperature to 700°C (BSM-1b, BSM-2b). In addition, an increase of sillenite Bi₁₂SiO₂₀ phase content is observed for BSM-2b (Bi:Si = 2:1, 700 °C) in comparison with BSM-1b (Bi:Si = 1:1, 700 °C). According to all of the obtained data, the increased amount of sillenite in BSM-2b can serve as the reason for the melting point at 805 °C for this sample (as shown on the DSC curve for the uncalcined BSM-2 sample) – due to the thermal instability of sillenite phases at increased temperatures [4].

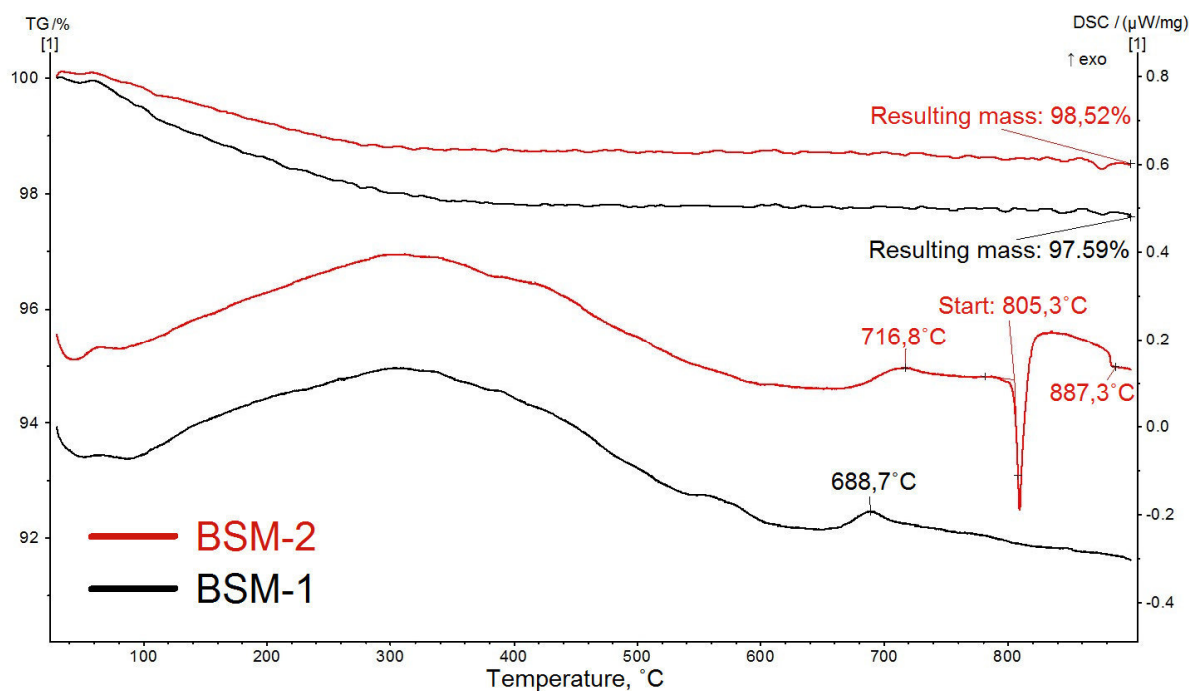


Fig. 1. TG-DSC curves for the uncalcined samples BSM-1 (Bi:Si = 1:1) and BSM-2 (Bi:Si = 2:1)

Table 1

Phase composition of the prepared bismuth silicates

Sample	Bi:Si atomic ratio	Calcination temperature, °C	Detected phases	Percentage, mass%	Coherent scattering region, nm
BSM-1	1:1	-	α -Bi ₂ O ₃	68	32
			SiO ₂ (quartz)	2	28
			SiO ₂ (coesite)	5	11
			Amorphous phase	25	-
BSM-1a	1:1	500	Bi ₂ SiO ₅	43	47
			Bi ₁₂ SiO ₂₀	31	41
			SiO ₂ (quartz)	26	16
BSM-1b	1:1	700	Bi ₄ Si ₃ O ₁₂	94	120
			Bi ₁₂ SiO ₂₀	6	18
BSM-2	2:1	-	α -Bi ₂ O ₃	50	42
			BiO ₂	10	10
			Bi ₂ O ₄	2	17
			SiO ₂ (coesite)	15	28
			Amorphous phase	23	-
BSM-2a	2:1	500	Bi ₂ SiO ₅	39	32
			Bi ₁₂ SiO ₂₀	57	72
			SiO ₂ (quartz)	4	-
BSM-2b	2:1	700	Bi ₄ Si ₃ O ₁₂	72	138
			Bi ₁₂ SiO ₂₀	28	51

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