
**MATERIALS OF POWER ENGINEERING
AND RADIATION-RESISTANT MATERIALS**

Synthesis of Stable Bismuth Silicate with Sillenite Structure in the $\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{SiO}_2$ System

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Abstract—A combined method for synthesizing a highly dispersed (0.8–2.5 μm) hydrophobic $\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{SiO}_2$ powder (NBS powder) based on solutions of sodium methyl silicate and bismuth nitrate is studied. The powder is synthesized at a reduced temperature (100°C). The microstructure and the phase composition of the resulting compounds in the $\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{SiO}_2$ system at different processing temperatures are investigated. The structural phase transformations in the mineral phases of NBS powder are revealed in the temperature range of 100–500°C. The metastable bismuth silicate Bi_2SiO_5 at 400°C is transformed into stable sillenite with composition $\text{Bi}_{12}\text{SiO}_{20}$ having a cubic crystal structure ($a = 10.1050 \text{ \AA}$). The synthesized NBS powder can be used as a filler to fabricate highly effective constructional radiation-shielding polymer composites with tailored properties.

Keywords: bismuth silicate, sillenite, synthesis, fineness, phase composition, structure, thermal treatment, phase transformations

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INTRODUCTION

Synthesis of highly dispersed oligomer–metal polymer fillers is a promising trend in designing highly efficient constructional radiation-shielding polymer composites with tailored properties [1–3].

The following requirements need to be fulfilled to synthesize a highly dispersed polymer matrix filler:

- (1) Powder particles should be monodisperse.
- (2) The powder particle size should not be greater than 5 μm .
- (3) The powders should be uniphase with respect to their mineral composition.

There is currently a keen interest in synthesizing bismuth-containing organomodified siloxanes. This interest is due to the fact that organosilicon compounds possess many valuable properties, such as high thermal stability, hydrophobicity, dielectric properties, and resistance to a number of aggressive media. Furthermore, bismuth atoms have a large gamma-ray absorption cross section, being hardly inferior to lead atoms in a broad energy spectrum [4]. The vacant $3d$ orbitals in silicon atoms are responsible for the high reactivity of the Si–OH bond in silicate minerals [5, 6].

Among various methods for synthesizing metal oligomers, researchers place special focus on the sol-

gel technology [5]. This method has a number of advantages, such as a high degree of homogenization of the resulting products, low synthesis temperatures, and, therefore, low energy expenditure and a simplified flow sheet. It is also promising to use water-soluble chemically active organosiloxanes and to produce metal oligomers using these compounds.

The known methods for synthesizing bismuth silicates with the sillenite structure are characterized by elevated synthesis temperature (at least 600°C) and duration (at least 24 h); furthermore, the materials produced are poorly compatible with the polymer matrix [7, 8].

This study aimed to develop a combined method for synthesizing a highly dispersed modified sillenite (bismuth silicate) from sodium methyl silicate and bismuth nitrate using the sol-gel process and to investigate the microstructure and the phase composition of the products in the $\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{SiO}_2$ system at different processing temperatures.

EXPERIMENTAL

Water–ethanol solution of sodium methyl silicate (SMS) $\text{H}_3\text{CSi}(\text{OH})_2\text{ONa}$ and solution of bismuth nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in acetone

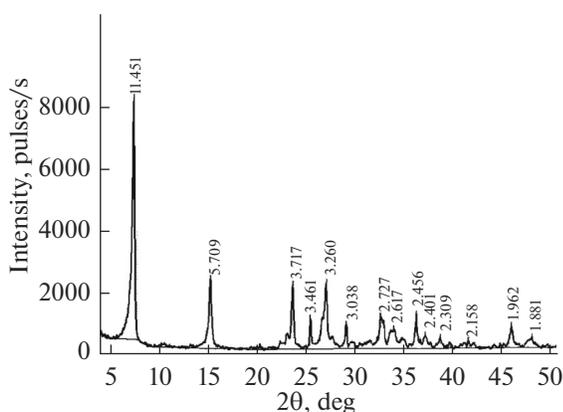


Fig. 1. X-ray diffraction pattern of the synthesized NBS material.

with nitric acid added were used to synthesize bismuth silicate in the $\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{SiO}_2$ system (NBS material). The amounts of the initial components calculated to obtain a stable bismuth silicate with composition $\text{Bi}_{12}\text{SiO}_{20}$ ($6 \text{ Bi}_2\text{O}_3 \cdot \text{SiO}_2$) were used.

Bismuth organosilicate powder was synthesized using the sol-gel technology by adding the acidified acetone solution of bismuth nitrate pentahydrate to the water-ethanol solution of sodium methyl silicate at 20°C under continuous stirring at specified concentrations of the components. The precipitate was centrifuged (5000 rpm) and washed with distilled water to remove water-soluble components (to reach pH 7). The 35% aqueous suspension was dried in a spray dryer at 100°C .

The resulting highly dispersed ($5-7 \mu\text{m}$) NBS material is insoluble in water, ethanol, acetone, benzene, and other solvents and is hydrophobic. The water contact angle of the NBS powder is 122°C , thus indicating that adsorption of the organosilicon oligomer (sodium methyl silicate) from the solution is positive and contributes to its uniform distribution over the outer surface of the resulting mineral phases.

The bulk density of the synthesized NBS powder was 2170 kg/m^3 ; its true density was 3780 kg/m^3 .

The phase composition of the mineral phases in the NBS material was studied by X-ray powder diffraction (XRD) analysis. The mineral crystalline phases were identified using the powder diffraction (PDF) database.

IR spectroscopy of the NBS powder was conducted on a VERTEX 70v Fourier transform infrared spectrometer in the spectral range of $400-2500 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The mass spectroscopy data showed that the NBS material had the following composition (on the oxide

basis): Na_2O , 23.83 wt %; Bi_2O_3 , 59.70 wt %; and SiO_2 , 16.47 wt %.

Three mixed amorphous + crystalline mineral phases were detected in the XRD patterns of the synthesized NBS material (Fig. 1, Table 1).

(1) Metastable bismuth silicate with composition $(\text{Bi}_2\text{O}_3 \cdot \text{SiO}_2) \text{ Bi}_2\text{SiO}_5$ ($d = 3.0379, 3.7169, 2.7223 \text{ \AA}$) crystallizing in the tetragonal crystal system ($a = 3.802 \text{ \AA}$; $c = 15.134 \text{ \AA}$) and having a mixed amorphous + crystalline structure with the amorphous halo $\sim 3 \text{ \AA}$ wide. Synthesis of this bismuth silicate is possible owing to chemical interaction (polycondensation) between the hydrated amorphous silica and bismuth hydroxide.

(2) Bismuth oxide $\alpha\text{-Bi}_2\text{O}_3$ ($d = 3.2596, 1.9625 \text{ \AA}$) crystallizing in the monoclinic crystal system ($a = 5.8499 \text{ \AA}$; $b = 8.1698 \text{ \AA}$; $c = 7.5123 \text{ \AA}$) having a mixed amorphous + crystalline structure with the amorphous halo $\sim 3 \text{ \AA}$ wide. The content of bismuth oxide in the NBS material according to the XRD data (compared to the reference bismuth oxide) was 22.4%.

(3) Bismuth organosilicate of tentative composition $\text{H}_3\text{C}(\text{Si}_x\text{Bi}_y\text{O}_z)\text{Na}$ having an amorphous halo $10-12 \text{ \AA}$ wide and a well-defined X-ray reflection at $d = 11.4513$ and 5.7090 \AA . However, this compound could not be precisely identified using the PDF powder diffraction database. This bismuth organosilicate could have potentially been formed via polycondensation between SMS and bismuth hydroxide.

Hence, the mineral phases formed in the NBS material at 100°C are amorphized to a significant extent. The width of the amorphous halo in the XRD patterns characterizes the average distance between the neighboring molecular chains [9]. For the sake of comparison, the peak position of the amorphous halo in sodium poly(methyl silicate) (dry residue of sodium methyl silicate at 100°C) was observed at $4-5 \text{ \AA}$.

As mentioned above, formation of bismuth oxide can be caused by dehydration of bismuth hydroxide that is precipitated during the synthesis of the NBS material. Since it is very unlikely that SMS interacts with bismuth nitrate in the solution, bismuth silicates are probably formed as a result of adsorption of SMS onto the surface of bismuth hydroxide from the solution followed by polycondensation via hydroxyl OH groups upon heating (100°C).

The IR spectrum of the NBS powder synthesized from the solutions in the $\text{SMS}-\text{Bi}(\text{NO}_3)_3$ system followed by drying at 100°C contains multiple narrow bands with sharp peaks that form complex and mainly asymmetric contours at $460-950 \text{ cm}^{-1}$ and $1250-1450 \text{ cm}^{-1}$ and diffuse, somewhat broadened contours at $100-1150 \text{ cm}^{-1}$ (Fig. 2). This shape of the IR spectrum attests to the well-formed crystal structure of the compound and presence of an amorphous silicate phase in it.

Table 1. X-ray parameters of the compound crystallized at different experimental temperatures in the synthesized NBS material

No.	Bragg angle 2θ , °	Interplane distance d , Å	Line intensity, %
Synthesized NBS material			
1	7.720	11.4513	100.00
2	15.520	5.7093	28.72
3	23.940	3.7169	26.92
4	27.360	3.2596	27.46
5	29.400	3.0379	10.26
6	32.900	2.7223	13.35
7	46.260	1.9625	9.06
Thermal treatment at 200°C			
1	7.700	11.4810	100.00
2	15.540	5.7020	30.11
3	23.940	3.7169	29.00
4	27.360	3.2596	42.41
5	29.380	3.0399	12.38
6	33.020	2.7127	22.00
7	46.340	1.9593	14.25
Thermal treatment at 300°C			
1	15.540	5.7020	6.10
2	24.980	3.5645	26.05
3	27.940	3.1932	100.00
4	29.360	3.0419	68.88
5	32.740	2.7352	34.18
6	37.260	2.4131	35.40
7	37.980	2.3690	13.53
Thermal treatment at 400°C			
1	16.760	5.2896	10.12
2	24.940	3.5701	15.66
3	27.920	3.1955	100.00
4	29.340	3.0440	26.68
5	32.700	2.7385	32.47
6	33.120	2.7047	24.23
7	37.940	2.3714	13.98
Thermal treatment at 500°C			
1	16.780	5.2833	21.63
2	24.920	3.5729	32.78
3	27.840	3.2045	100.00
4	29.340	3.0440	60.48
5	33.140	2.7031	66.84
6	37.780	2.3811	18.49

The IR spectrum features closely located absorption bands corresponding to bending vibrations of the Si–O–Bi bond at 430, 475, 540, 685, and 860 cm^{-1} ; bending vibrations of the Si–O bond at 705 cm^{-1} ; stretching vibrations of the Si–O–Si bond at 1030 and 1060 cm^{-1} ; stretching vibrations of the Si–O–Na

bond at 935 cm^{-1} ; bending vibrations of the Si–OH bond at 870 cm^{-1} ; stretching vibrations of the Si–CH₃ bond at 1260 cm^{-1} ; stretching vibrations for carbonate ions CO₃²⁻ at 1450 cm^{-1} ; and bending vibrations of adsorbed water molecules at 1640 cm^{-1} (in accordance with [10]).

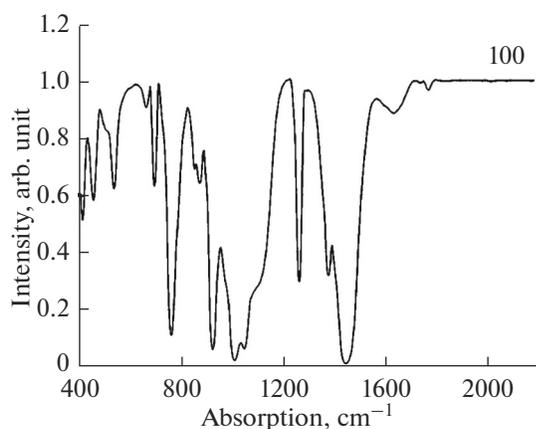


Fig. 2. IR spectrum of the synthesized NBS material.

The shape of the absorption bands corresponding to bending and stretching vibrations of water in the IR spectrum at 1600–1700 cm^{-1} demonstrates that hydroxyl groups OH are a structurally bound component in siloxanes.

According to the IR spectroscopy data, the silicate phases in the synthesized NBS material powder have a

linear structure. Splitting of absorption bands in the region of 1000–1100 cm^{-1} , which is typical of the siloxane bond, attests that several types of siloxane phases exist.

No new mineral phases were revealed when the NBS powder was subjected to thermal treatment at 200°C (Fig. 3a). According to the XRD data, the content of bismuth organosilicate of tentative composition $\text{H}_3\text{C}(\text{Si}_x\text{Bi}_y\text{O}_z)$ decreases by ~60% ($d = 11.4810 \text{ \AA}$, $I = 100\%$) because of thermal destruction (oxidation of CH_3 methyl groups in silicate) and subsequent amorphization of the organosilicate with the amorphous halo at $d = 11 \text{ \AA}$.

The intensity of reflections for bismuth silicate of composition Bi_2SiO_5 ($d = 3.0399 \text{ \AA}$, $I = 100\%$) in the XRD patterns decreases, which is probably due to further amorphization of the crystal with the amorphous halo at $d = 3.3 \text{ \AA}$.

X-ray characteristics and the crystallographic structure for bismuth oxide $\alpha\text{-Bi}_2\text{O}_3$ do not change, while the reflection intensity in the XRD pattern decreases (Fig. 3a, Table 1). The content of bismuth oxide in the NBS material evaluated using the XRD data decreases to some extent (to 21.3%).

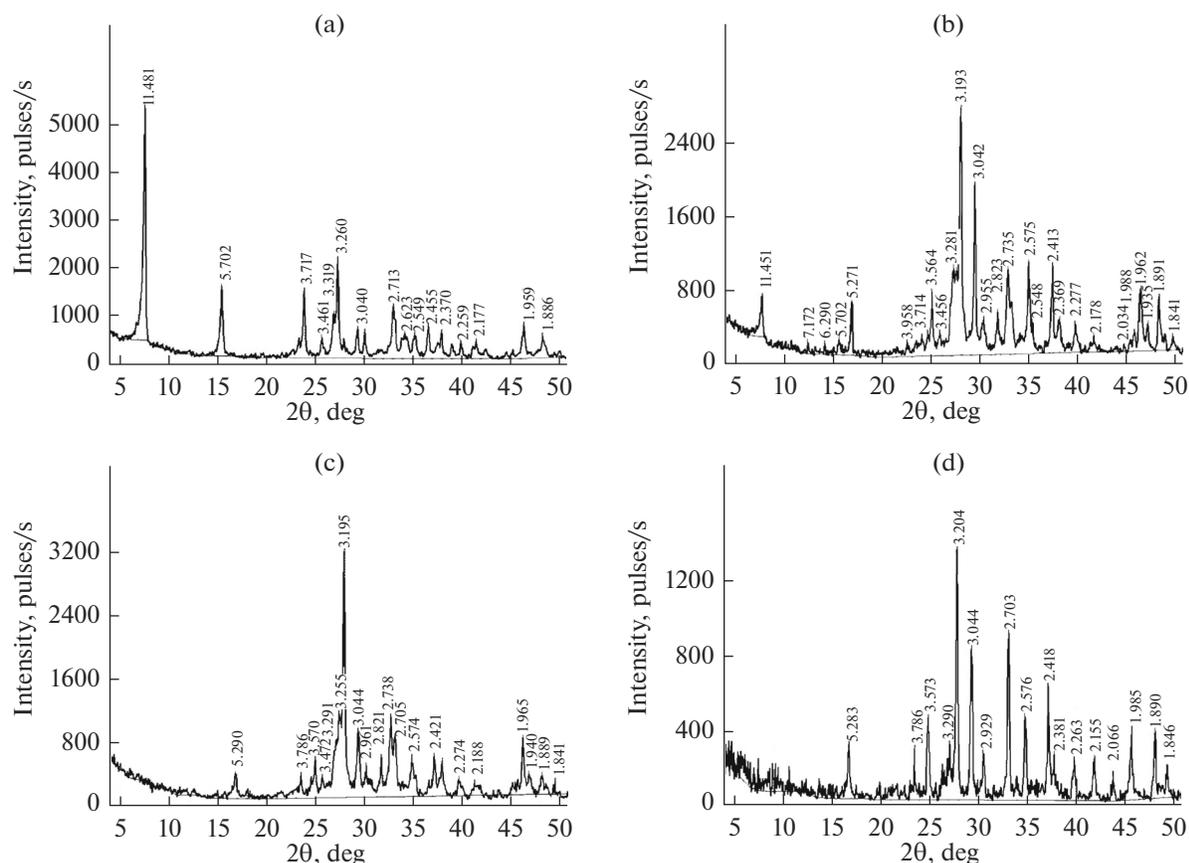


Fig. 3. XRD pattern of the NBS material processed at (a) 200°C, (b) 300°C, (c) 400°C, and (d) 500°C.

Thermal treatment of the NBS material at 300°C gives rise to a new mineral phase, sodium metasilicate Na_2SiO_3 crystallizing in hexagonal crystal system ($d = 3.0419, 3.5645, 2.4131 \text{ \AA}$ with $[\text{SiO}_3]_{\infty}^{2-}$ chains), which is probably formed owing to thermal destruction of organosiloxane of composition $\text{H}_3\text{C}(\text{Si}_x\text{Bi}_y\text{O}_z)_n\text{Na}$. A transition between metastable bismuth silicate of composition Bi_2SiO_5 crystallizing in tetragonal crystal system and bismuth silicate of composition $\text{Bi}_{12}\text{Si}_{0.87}\text{O}_{20}$ crystallizing in cubic crystal system ($d = 3.1932, 2.7352 \text{ \AA}$) was detected. The reflection intensity for bismuth organosilicate of composition $\text{H}_3\text{C}(\text{Si}_x\text{Bi}_y\text{O}_z)_n\text{Na}$ in the XRD pattern (Fig. 3b, Table 1) also decreased abruptly. Reduction in reflection intensities in the XRD patterns (up to 20.0%) was also observed for bismuth oxide $\alpha\text{-Bi}_2\text{O}_3$.

Thermal treatment at 400°C gives rise to a new mineral phase, stable bismuth silicate of composition $\text{Bi}_{12}\text{SiO}_{20}$ ($6 \text{ Bi}_2\text{O}_3\text{SiO}_2$) crystallizing in cubic crystal system ($d = 3.1955 \text{ \AA}$ with high-intensity reflections in the XRD pattern: $d = 3.5701, 2.7047 \text{ \AA}$) with the lattice parameter $a = 10.1050 \text{ \AA}$. Formation of this bismuth silicate is probably caused by structural rearrangement of metastable bismuth silicate of composition $\text{Bi}_{12}\text{Si}_{0.87}\text{O}_{20}$ (not detected in the XRD pattern, Fig. 3c, Table 1).

According to the XRD data, the content of bismuth oxide in the NBS material decreased almost twofold, to 10.3%. The intensity of reflections for sodium metasilicate Na_2SiO_3 was also noticeably reduced (by a factor of 2.3). Bismuth organosilicate $\text{H}_3\text{C}(\text{Si}_x\text{Bi}_y\text{O}_z)_n\text{Na}$ was not detected in the XRD pattern, demonstrating that it underwent complete thermal destruction at 400°C.

Thermal treatment at 500°C significantly increased the intensity of reflections in the XRD pattern of stable bismuth silicate of composition $\text{Bi}_{12}\text{SiO}_{20}$ (at $d = 3.2045 \text{ \AA}$). The content of sodium metasilicate Na_2SiO_3 in the NBS material became stabilized, while no bismuth oxide was detected (Fig. 3d, Table 1).

The mineralogical composition of the NBS material thermally treated at 500°C was determined by pycnometric and X-ray diffraction analyses: bismuth silicate $\text{Bi}_{12}\text{SiO}_{20}$, 81.93 wt %; sodium metasilicate Na_2SiO_3 , 18.07 wt %.

Further thermal studies demonstrated that the material had a stable phase composition at temperatures up to 650°C. The resulting bismuth silicate of composition $\text{Bi}_{12}\text{SiO}_{20}$ with the cubic crystal lattice was gray.

Figure 4 shows the scheme of phase transformations in the $\text{SMS-Bi}(\text{NO}_3)_3\text{-HNO}_3$ system in the temperature range of 100–500°C.

The IR spectrum of the NBS sample subjected to thermal treatment at 500°C did not feature the absorption band for the (Si-CH_3) bond at 1260 cm^{-1} , being indicative of complete destruction of methyl radicals in the siloxane bond. Meanwhile, the spectrum fea-

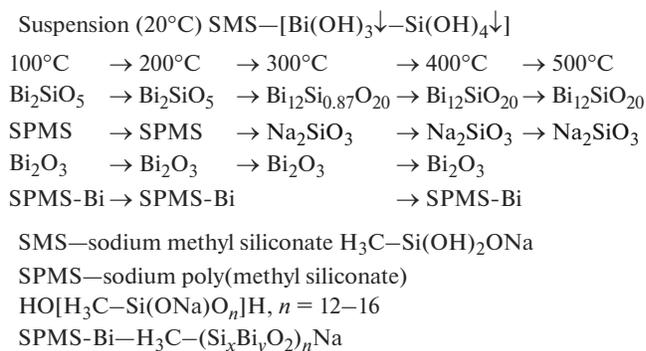


Fig. 4. The scheme of phase transformations in the $\text{SMS-Bi}(\text{NO}_3)_3\text{-HNO}_3$ system in the temperature range of 100–500°C.

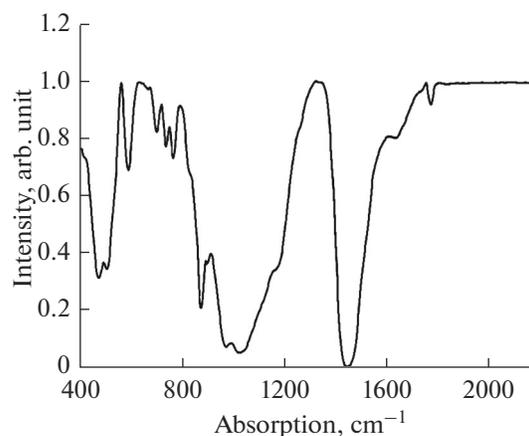


Fig. 5. IR spectrum of the NBS material processed at 500°C.

tured many narrow and high-intensity absorption bands corresponding to bending vibrations of the metal–siloxane bond (Si-O-Bi) at $450\text{--}750 \text{ cm}^{-1}$ (Fig. 5).

The principal absorption band of stretching vibrations of the siloxane bond at $1000\text{--}1100 \text{ cm}^{-1}$ is broadened, indicating that the silicate phases are amorphized to some extent. Disappearance of the absorption doublet at 1030 and 1060 cm^{-1} in this region of the IR spectrum, which is typical of the initial sample (100°C), and detection of one intense absorption band at reduced frequencies (1030 cm^{-1}) are indicative of rearrangement of the structure of the silicate (sodium metasilicate) and bismuth silicate phases (sillenite of composition $\text{Bi}_{12}\text{SiO}_{20}$) as a result of polycondensation and solid-state reactions in the $\text{Na}_2\text{O-Bi}_2\text{O}_3\text{-SiO}_2$ system at 500°C.

The emergence of a high-frequency absorption band at 1180 cm^{-1} in the IR spectrum indicates that chain silicate structures were formed in the sample. The absorption band (Si-O-Na) at 935 cm^{-1} is not

recorded in the IR spectrum as this band potentially overlaps the broadened absorption band corresponding to stretching vibrations of the siloxane bond at 900–1100 cm^{-1} .

The content of structurally bound water in the sample of NBS material subjected to thermal treatment at 500°C decreases abruptly as evidenced by reduction in absorption intensity at 1640 cm^{-1} .

CONCLUSIONS

Highly dispersed (0.8–2.5 μm) hydrophobic powder $\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{SiO}_2$ (NBS powder) based on solutions of sodium methyl silicate and bismuth nitrate was synthesized for the first time at reduced temperature (100°C). The NBS powder is multiphase: it contains modified bismuth silicate of composition Bi_2SiO_5 crystallizing in the tetragonal crystal system ($a = 3.802 \text{ \AA}$; $c = 15.194 \text{ \AA}$), bismuth (III) oxide crystallizing in the monoclinic crystal system ($a = 5.8499 \text{ \AA}$; $b = 8.1698 \text{ \AA}$; $c = 7.5123 \text{ \AA}$) and having a mixed amorphous + crystalline structure with the amorphous halo $\sim 3 \text{ \AA}$ wide, and the new crystalline phase, bismuth organosilicate, which has not been deposited in the PDF X-ray database.

The structural phase transformations in the mineral phases of the NBS powder were revealed in the temperature range of 100–500°C. Crystals of sodium metasilicate Na_2SiO_3 with continuous chain radicals $[\text{SiO}_3]^{2-}$ are formed at 300°C. At 400°C, the metastable bismuth silicate of composition Bi_2SiO_5 is transformed into stable sillenite of composition $\text{Bi}_{12}\text{SiO}_{20}$ having a cubic structure ($a = 10.1050 \text{ \AA}$).

The synthesized NBS powder can be used as a filler to fabricate highly efficient constructional radiation-shielding polymer composites with tailored properties.

REFERENCES

1. Pavlenko, V.I., Yastrebinskaya, A.V., Pavlenko, Z.V., and Yastrebinskii, R.N., Fine dispersed organosiloxane fillers of polymer matrices, *Izv. Vyssh. Uchebn. Zaved., Sev.-Kavk. Reg., Tekh. Nauki*, 2010, no. 2, pp. 99–103.
2. Pavlenko, V.I. and Yastrebinskii, R.N., Thermoplastic constructional composites for radiation protection, *Perspekt. Mater.*, 2010, no. 6, pp. 22–28.
3. Pavlenko, V.I., Yastrebinskii, R.N., and Edamenko, O.D., Radiation-protective metal-oligomeric filler for polymeric aggregates, *Vestn. Belgorod. Gos. Tekhnol. Univ.*, 2011, no. 2, pp. 117–120.
4. Mashkovich, V.P., *Zashchita ot ioniziruyushchikh izluchenii. Spravochnik* (Protection Against the Ionizing Radiation: Handbook), Moscow: Energoatomizdat, 1995.
5. Milinchuk, V.K., *Makroradikaly* (Macroradicals), Moscow: Khimiya, 1980.
6. Andrianov, K.A., *Kremniorganicheskie soedineniya* (Organic Silicon Compounds), Moscow: Khimiya, 1975.
7. Shlegel, V.N. and Pantsurkin, D.S., Growth of $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$ crystals by the low-thermal gradient Czochralski technique, *Crystallogr. Rep.*, 2011, vol. 56, no. 2, pp. 339–344.
8. Klebanskii, E.O., Kudzin, A.Yu., Pasal'skii, V.M., Plyaka, S.N., Sadvokaya, L.Ya., and Sokolyanskii, G.Kh., Thin sol-gel bismuth silicate films, *Phys. Solid State*, 1999, vol. 41, no. 6, pp. 913–915.
9. Pan'kov, G.N., *Radiatsionnaya modifikatsiya polimernykh materialov* (Radiation Modification of Polymeric Materials), Kiev: Tekhnika, 1969.
10. Smith, A.L., *Applied Infrared Spectroscopy: Fundamentals, Techniques, and Problem Solving*, Chichester: Wiley, 1979.

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