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## Bismuth silicates prepared via mechanochemical activation for photocatalytic applications

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Bismuth silicates are a family of compounds which is classified as complex oxide systems. Bismuth metasilicate  $\text{Bi}_2\text{SiO}_5$  is a substance of Aurivillius family with perovskite-type structure. At the same time, the structure of bismuth orthosilicate  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  is transitional from perovskite-type to framework, while the one of sillenite  $\text{Bi}_{12}\text{SiO}_{20}$  is purely a framework similar to  $\gamma\text{-Bi}_2\text{O}_3$ . These structural differences provide a sufficiently broad range of peculiar physical and chemical properties. For example,  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  can be used as potential scintillator material [1] due to lower production cost than that of bismuth orthogermanate  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , while having otherwise similar parameters. Up to the current date, there are several new reports, which also indicate on high potential of different bismuth silicate compositions in photocatalytic applications [2, 3].

In this work, environmentally friendly mechanochemical activation was applied, available to carry out the process with great speed in the absence of any solvent. With this method of synthesis, the influence of molar ratio of initial reagents on phase composition and properties of prepared samples was investigated.

For the first time, bismuth silicates were obtained via mechanochemical activation followed by calcination. Bismuth oxide  $\text{Bi}_2\text{O}_3$  and hydrous silica  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  were used as precursors. The stoichiometric mixtures with different composition were activated in a high-power planetary ball mill AGO-2 for 10 min [4]. The mixtures activated for 10 min were calcined at different temperatures for 2 h, with calcination temperatures being chosen with accordance to the data of TG-DSC.

Combined analysis of XRD and TG-DSC data shows that the initial molar ratio of  $\text{Bi}_2\text{O}_3\text{:SiO}_2 = 6\text{:}1$  ultimately leads to the formation of  $\gamma\text{-Bi}_{12}\text{SiO}_{20}$ , which decomposes at 875 °C. The formation of  $\text{Bi}_2\text{SiO}_5$  phase (primary) and  $\gamma\text{-Bi}_{12}\text{SiO}_{20}$  (impurity) is indicated in the sample with the molar ratio of  $\text{Bi}_2\text{O}_3\text{:SiO}_2 = 1\text{:}1$  in the course of calcination of mixtures activated at 500°C. At 600°C metastable  $\text{Bi}_2\text{SiO}_5$  phase is partially transformed to  $\text{Bi}_4\text{Si}_3\text{O}_{12}$ . With the molar ratio of  $\text{Bi}_2\text{O}_3\text{:SiO}_2 = 2\text{:}3$ , at 500 °C two modifications of  $\text{Bi}_2\text{SiO}_5$  phase are formed at the same time as  $\text{Bi}_4\text{Si}_3\text{O}_{12}$ . At 600 °C bismuth metasilicate phase completely transforms to  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  phase with the formation of  $\gamma\text{-Bi}_{12}\text{SiO}_{20}$  phase as impurity.

Photoluminescence effect was detected for all samples containing  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  phase, with the excitation peak at 250 nm. Other materials do not possess photoluminescence effect at all. UV-VIS diffuse reflectance spectroscopy data shows that prepared bismuth silicates absorb visible light and with accordance to XRD data possess different phase composition.

As shown above, mechanochemical activation for 10 min does not allow to synthesize single phase samples with molar ratio of  $\text{Bi}_2\text{O}_3\text{:SiO}_2 = 1\text{:}1$  and 2:3. Apart from expected stoichiometric phases, other phases of bismuth silicates are also detected. Multiphase composition can possibly be attributed to complex mechanisms of nuclei formation in the course of solid state reactions.

A photocatalytic study of all prepared materials in the reaction of Rhodamine B photodecolorization is expected. Additionally, a series of bismuth silicates prepared via conventional hydrothermal method will be discussed in the study, investigated with the methods described above to provide comparison.

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