

Effect of Air Annealing on Structural, Textural, Thermal, Magnetic and Photocatalytic Properties of Ag-Doped Mesoporous Amorphous Crystalline Nanopowders Bi_2O_3

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Abstract

Ag doped Bi_2O_3 nanopowders (NPs) were produced by pulsed electron beam evaporation (PEBE) under vacuum. The solid phase synthesis in an electric furnace on air was used for silver doping of bismuth oxide (addition of - 1 and 5 wt% crystalline silver nitrate). Structural, textural, thermal and magnetic properties of Ag doped Bi_2O_3 NPs have been studied. The specific surface area of (SSA) Ag- Bi_2O_3 NPs was 23.7 m²/g, which was almost 2 times bigger than the SSA of the pure Bi_2O_3 (13.2 m²/g). Air annealing (200 °C) caused decreased crystallinity and growth of SSA in all NPs, without exception. Silver doping reduced the grain size of NPs after they were air annealed compared to the grain size of NPs annealed pure bismuth oxide. The dominant phase in not annealed/annealed Ag doped Bi_2O_3 NPs at 200 °C and 300 °C was β -phase Bi_2O_3 with a tetragonal structure. Accordingly, the photocatalytic activity of the Ag doped NPs was higher in the doped Bi_2O_3 . The thermal stability of the pure and Ag-doped Bi_2O_3 NPs was maintained at 300-350 °C. The phase transition $\beta \rightarrow \alpha$ occurred with a further increase in temperature. The annealing temperature could effectively change the physicochemical properties of the Bi_2O_3 NPs.

1. Introduction

Bismuth containing compounds are promising for creating photocatalysts based on them using a visible range of light, and the simplest of bismuth-Bi₂O₃ oxides is most often used for that [1, 2]. Strong polymorphism (at least 9 polymorphic phases of Bi₂O₃ are known), thermal instability and change in the properties of bismuth oxide during long-term storage greatly complicates the study of its characteristics [3, 4]. Bi₂O₃ with the desired properties were prepared using various methods such as solution crystallization, sol-gel, thermal evaporation and thermal oxidation, microwave [5-8], etc. Often, to improve stability and enhance photocatalytic properties, doping of Bi₂O₃ with various metals is used [9-11], in particular Aq, which has bactericidal properties [12–14] and leads to the appearance of plasmon resonance [15-16]. Typically, chemical methods using toxic chemicals are used to prepare Ag doped Bi₂O₃ nanoparticles (NPles) [17, 18]. Among other techniques, the pulsed electron beam evaporation (PEBE) method allows the production of various high purity nanomaterials under vacuum without the use of chemical reagents [19, 20]. The α - phase Bi₂O₃ is thermodynamically stable at room temperature, the δ phase is stable at high temperature, the remaining phases are metastable. When heated in air, vacuum and various gases, a wide palette of phase transformation paths of various Bi₂O₃ polymorphs was observed, depending on the phase composition of the starting material and a number of other experimental parameters inherent in each particular NPles production method [21, 22]. It is known that the tetragonal β -phase Bi₂O₃ has the maximum photocatalytic activity among all polymorphic phases of Bi_2O_3 [23, 24]. However, the thermodynamic stability of the β phase is limited by a temperature of about 400 ° C [25]. Doping Bi₂O₃ with various elements [26, 27], in particular Ag [28-30], has been widely used to stabilize metastable β-phase at room temperature. Low-toxicity NPles Bi₂O₃ with small Ag additives

are promising for use in photocatalysis [31–33] and in various biomedical applications, in particular, in cancer cell therapy [34–36].

The purpose of this work was to examine the effect of annealing for 30 min at (200 °C, 300 °C, 500 °C, 750 °C) on the structural, thermal, textural, magnetic and photocatalytic properties of the synthesized by PEBE method Ag doped Bi₂O₃ NPles. Knowledge of the evolution of the main physicochemical characteristics of Ag doped Bi₂O₃ NPles after annealing in the air allows us to purposefully select and use annealed NPles in various fields of science and technology, in which specific requirements for NP are imposed for their practical use.

2. Materials

Oxide bismuth (III) micron powder (Bi_2O_3), analytic grade, GOST 10216-80 and silver nitrate (AgNO₃) of HC grade, GOST 1277-75 were used to obtain Ag doped- Bi_2O_3 NPs.

2.2. Synthesis of Ag doped Bi₂O₃ NPs in vacuum

Ag doped Bi_2O_3 electron beam evaporation targets were prepared according to the following procedure: AgNO₃ crystals were pre-ground in a porcelain mortar and then mixed with micron powder Bi_2O_3 at the following weight ratios- Bi_2O_3 : AgNO₃ = 99:1 and 95:5. Further, compacts were made from mechanical mixtures, which were then annealed at a temperature of 500–600 ° C in air for 30 minutes (the decomposition temperature of the AgNO₃ is 350 ° C [37]), followed by cooling the compacts together with the furnace to room temperature. The annealed compacts were re-ground in a mortar to more evenly distribute the silver in the mixtures. From the crushed powders, targets were re-made on a hand press in a titanium mold. The diameter of the targets was 40 mm, height up to 1-1.5 mm, weight about 60 g. The targets were heated in air to a temperature of 500–600 ° C for 30 minutes and then cooled together with the furnace to room temperature.

Evaporation mode Ag doped Bi_2O_3 targets: accelerating voltage-38 kV, beam current-0.1 A, pulse duration-100 µs, pulse frequency-50-100 Hz, beam scanning on the target surface-12 cm², NP collection (excluding losses) at evaporation time of 30 min. -2.5 g (sample S1) and – 3.6 g (sample S5).

NP deposition was carried out on conventional windows located at a distance of 10–15 cm relative to the center of the target. The NP was collected using a titanium foil scraper. NPs had very little adhesion to glass substrates and steel surfaces. NP color - black-gray (sample S1) and black (sample S5).

A general scheme for the synthesis of Ag-doped Bi_2O_3 NPs from raw material micron Bi_2O_3 powders and AgNO₃ crystals using the PEBE vacuum method is shown in Fig. 1.

2.3. Characterization

X-ray diffraction studies were carried out using a high-resolution X-ray diffractometer "Empyrean" in copper filtered radiation at the collective use center "Test Center for Nanotechnology and Advanced Materials" of the Institute of Metal Physics of the Ural Branch of the Russian Academy of Sciences (Department of X-ray Diffraction Analysis). PANanalytical's PIXcel 3D counter was used (step 0.026 degrees). Parameters were calculated using PowderCell and HighScore Plus 4.1 software. The Williamson-Hall method was used to determine the values of coherent scattering regions (CSR) and stresses of the 2nd kind. Micromerics TriStar 3000 V6.03 A was used to record nitrogen adsorption and desorption isotherms at 77 K. Synchronous thermoanalytic complex NETZSCH STA-409 was used in thermal analysis of samples. The transmission electron microscopy (TEM) was employed to study the morphological and structural features of synthesized Ag doped Bi₂O₃ NPles. Faraday scales were used for magnetic measurements of specific magnetization at room temperature. The silver content in the Ag doped Bi₂O₃ samples was determined using a Pekrin Elmer mass spectrometer. The photoluminescence spectra were recorded from 500 nm to 650 nm on an MDR-204 monochromator. The catalytic activity of air-annealed Ag-doped Bi₂O₃ NPs was evaluated by photodegradation of an aqueous solution of methyl orange (MO). Irradiation of aqueous suspensions of NPs with MO dye was carried out using ultraviolet gas discharge lamp DRSh 250-3 (250 W), luminous flux - 13,000 lm. MO was dissolved in distilled water, then a photocatalyst was added and the suspension was irradiated with a UV lamp for 40 minutes. The photocatalyst was uniformly distributed by ultrasonic treatment of the slurry in an ultrasonic bath PSB-2828-05 for 5 minutes at room temperature. Every five minutes of irradiation, an aliquot of the 4 ml solution was taken into a quartz cuvette. The concentration of MO in the suspensions was measured using a spectrophotometer PE-5400UF, for which the absorbance was measured at a wavelength of 595 nm.

3. Results and discussion

3.1. Structural analysis and morphology of synthesized Ag doped Bi_2O_3 NPs

3.1.1. XRD analysis

On **Fig.2**, diffractograms of not annealed samples S0, S1 and S5 are shown. A detailed description of the diffractogram of sample S0 is given earlier in **[19, 20]**. S0 contained two crystalline phases in a ratio of $\beta:\alpha=84:16$ to an amorphous component (about 50-60% by volume). On all three diffractograms on **Fig. 2**, a wide, amorphous peak was present near the 20 angle ~ 29.30. Silver-containing samples of S1 and S5 also contained a small amount of amorphous fraction not exceeding 10-15% of the sample volume.

The main crystalline phase found in samples S0, S1 and S5 is the β phase of the Bi₂O₃ with a tetragonal lattice, a structure of the type Bi₂O₃ Sillenite space. group P-4b2. **[38]**. Samples S1 and S5, in addition to the amorphous phase and diffraction lines from β -phase Bi₂O₃, showed a weak peak from an unidentified phase (shown in **Fig. 2** with the red arrow). This peak coincides, for example, with the main reflection

(121) of the monoclinic phase of the Bi_2O_3 type Dibismuth Trioxide - R, space. rpynna P1 21/c1 (14) **[39]** or hexagonal type Dibismuth Trioxide - Hp Bi_2O_3 , ex. Group P31c (159) **[40]**. However, it is not possible to confidently associate the marked peak with the two above mentioned phases, since other reflections characteristic of these phases could not be detected. Near the position of the diffraction line of unknown phase there may also be a characteristic cubic bismuth intense line **[41]**, however, and in this case there should be a second line with d ~ 2.246, Θ (~ 40.1 deg 2 Θ), which was not observed in the diffractograms on the **Fig.2**. A comparison of the diffractograms of the S1 and S5 samples showed that they were almost the same, a clear difference was observed only in the relative intensity of the peak of the unknown phase. Peak intensity from the unknown phase increased with increasing silver concentration in the sample. The increase in intensity could indicate that the composition of the unknown phase contained Ag. However, we could not find in our X-ray structures database a compound with Ag, Bi and/or O having such a reflection.

Fig. 3 shows diffractograms of an Ag-free sample S0 annealed in air at temperatures of 200, 300, 500 and 750 °C. The corresponding samples are designated-S200, S300, S500 and S750. Sample S0 underwent a significant transformation as a result of annealing according to the scheme



The change in color of the samples with an increase in annealing temperature (NP color samples are shown on the inserts to each diffractogram on the **Fig.3-Fig.5**) correlates well with the phase transformation of sample S0 during the air annealing process. A distinctive feature of phase transformations during annealing of sample S0 was the formation of bismuth carbonate $Bi_2O_2CO_2$, which was not detected in Ag-doped Bi_2O_3 NPs samples.

Fig 4,5 shows diffractograms of Ag doped Bi₂O₃ samples of S1 and S5 annealed in air at 200, 300 and 500 °C, with different silver concentrations. According to the (Inductively Coupled Plasma Mass Spectrometry) ICP-MS analysis, the Ag concentration in the S1 and S5 samples was 0.60 and 2.36 wt%, respectively. In doped samples S1, S5 and not doped sample S0, the iron content was less than 0.005 wt%.

Samples S1 and S5 annealed in air are referred to as S2001, S3001, S5001 and S2005, S3005, S5005, respectively.

On the diffractograms of the S1 and S2001 samples, the peak from the unidentified phase was quite clearly visible. On the diffractogram of the sample S3001 only upon careful examination could a weak

trace of reflection from an unknown phase be seen. Halo from the amorphous component was practically not visible. Only monoclinic S5001 -phase (space) was observed in the α sample. Group P1 21/c1 (14) **[42]**. The disappearance of the halo from the amorphous phase and the decrease in peak intensity from the unknown phase indicated crystallization of the amorphous component and possible dissolution of excess silver in the tetragonal lattice Bi₂O₃ at an annealing temperature of 300 °C.

On the diffractograms of the samples S5 and S2005 (**Fig. 5**) a halo from amorphous fraction and a peak from an unidentified phase were also present. The peak intensity from the unknown phase was significantly greater than that of the respective S1 and S2001 samples. In the sample diffractogram, the S3005 peak from the unknown phase is also almost not visible. The S5005 sample as well as the S3001 sample contained only the α phase of the Bi₂O₃.

Comparison of diffractograms shown in **Fig. 4** and **Fig. 5** showed that they were essentially the same, the main difference being only the relative intensity of the peak from the unknown phase.

Thus, the silver-containing samples annealed in air, regardless of the concentration of silver introduced, were found to be structurally identical. The dominant phase in the not annealed and annealed at 200 and 300 ° C was β -phase Bi₂O with a tetragonal structure. All samples, regardless of Ag concentration, contained small impurities of an amorphous phase and an unidentified phase. All samples annealed at 500 ° C consisted of monoclinic α phase Bi₂O₃. In **Table 1**, X-ray diffraction parameters of samples of pure Bi₂O₃ and Ag-doped Bi₂O₃ NPs annealed in air are given. The data given in **Table 1** shows that the doping of Ag led to an increase in grain size in not annealed samples from 8-10 nm to 20-25 nm, and further annealing at a temperature of 300 ° C caused the growth and alignment of grain size in samples with different silver concentrations to the same value equal to 41 nm.

Parameters of hexagonal and monoclinic phase lattices in both batches of silver-containing samples differed slightly.

Table 1. X-ray diffraction parameters of samples of pure Bi_2O_3 and Ag-doped Bi_2O_3 NPs annealed in air.

Undoped Bi ₂ O ₃					
S0	β	a = 7.728, c = 5.625	84	8-10	
	α		16		
	amorph		50-60 % V		
S200	β	a = 7.757 c = 5.661	28	~40	
	Bi ₂ O ₃ CO ₂	a = 3.884 b = 3.866 c = 13.793	72	~80	
S300	β	a = 7.752 c = 5.674	~13.0	?	
	Bi ₂ O ₃ CO ₂	a = 3.889 b = 3.867 c = 13.758	83.5	?	
	α	a = 5.880 b = 8.183 c = 7.497	3.5	?	
		beta(deg) = 112.63			
S500	α	a = 5.869 b = 8.200 c = 7.534	100%	> 300	
		beta(deg) = 112.93			
Ag doped Bi ₂ O ₃ (1 wt.% AgNO ₃)					
S1	β	a= 7.748 c = 5.652	?	22/0.1	
S2001	β	a= 7.752 c = 5.664	?	34/0.1	
S3001	β	a= 7.756 c = 5.665	?	41/0.15	
S5001	α	a= 5.845 b = 8.160	?	71/0.02	
		c = 7.505 β = 113.00°			
Ag doped Bi ₂ O ₃ (5 wt.% AgNO ₃)					
S5	β	a= 7.752 c = 5.658	?	25/0.1	
S2005	β	a= 7.754 c = 5.660	?	10/0.1	
S3005	β	a= 7.756 c = 5.665	?	41/0.15	
S5005	α	a= 5.846 b = 8.161	?	>150/0.05	
		c = 7.506 β = 113.00°			

Error ±0.002

Annealing the samples at 500 °C further increased the grain size growth in the samples, for example, the grain size in the sample S5005 increased 2-fold (> 150 nm) than the grain size in the sample S5001 (71 nm). Most notably, the annealing temperature affected the grain size growth of the not doped sample S0. After annealing at a temperature of 500 ° C, the grain size of the not doped sample S0 significantly exceeded (> 300 nm) the corresponding grain sizes of the silver-containing samples.

Thus, silver doping significantly reduced the grain size growth in Ag doped Bi₂O₃ NPs when annealed in air, relative to the corresponding grain size growth in annealed not doped NPs Bi₂O₃

3.1.2. TEM and HRTEM analysis

The change in the morphology of the non doped S0 sample during air annealing up to 750 ° C was discussed in detail in our early works **[19, 20]**. The initial multiphase amorphous crystal sample S0 was transformed into a single phase α -Bi₂O₃ sample during annealing when the annealing temperature reached 500 °C. The main morphological feature in the annealing of sample S0 was the presence of amorphous crystalline nanoclusters of about 3-5 nm, which were present in the original sample S0 and remained in annealed samples up to 750 °C. Looking ahead, nanoclusters of 3-5 nm were also present in Ag doped samples S01 and S05 when annealed to 300 °C. At an annealing temperature of 500 °C, the samples were sintered and were formed sub-micron particles without nanoclusters.

TEM и HRTEM images исходных и отожженных образцов S1 и S5 приведены на **Fig.7** and **Fig. 8**, соответственно. На вставках **Fig. 7(a,b,c,d)** and **Fig.8 (a,b,c,d)** приведены selected area electron diffraction (SAED) исходных и отожженных образцов S1 и S5.

TEM and HRTEM images of the initial and annealed S1 and S5 samples are shown in **Fig.7** and **Fig. 8**, respectively. On inserts **Fig. 7 (a, b, c, d)** and **Fig.8 (a, b, c, d)** are selected area electron diffraction (SAED) of initial and annealed samples S1 and S5.

Ag-doped samples had the similar morphology. Amorphous and crystalline nanodroplets of about 3-5 nm were also present in silver-doped S1 and S5 samples, as in the non doped S0 sample. However, annealing samples have different effects on the crystallinity of the samples. It follows from SAED images of sample S0 (Fig.6 (a, b, c, d)) that as the annealing temperature increased, the degree of crystallinity of the sample increased (ring diffraction patterns (samples S0, S200 and S300) transformed eventually into spot diffraction pattern S500), which was caused by the growth of crystal size due to sintering and coalescence of NPles. However, the change in crystallinity of sample S0. First, the comparison of electron diagrams of unannealed S0, S1 and S5 samples (Fig.6a,7a,8d) clearly shows that the degree of crystallinity increased with the increase in silver concentration in the samples (the number and size of point reflexes on SAED images increased with the increase in silver concentration). Second, annealing at 200 °C resulted in attenuation of crystallinity in the S2001 and S2005 samples, as evidenced by blurred ring reflexes on the corresponding SAED images on Fig.7b and Fig.8b. A further increase in annealing temperature caused an increase in the crystallinity of both annealed samples S1 and S5, however, the

crystallinity of the sample S1 increased faster than that of the S5 sample. On the SAES image of the S3001 sample (**Fig.7c**) are present point reflexes from single crystals and on the SAED image of the S3005 sample (**Fig.8f**) are present point and ring reflexes, indicating the polycrystalline structure of the S3005 sample.

TEM (Fig.7g) and HRTEM (Fig. 7k) images clearly prove the formation of crystals with perfect crystal structure in a sample with a low concentration of Ag. A further increase in annealing temperature to 500 °C resulted in a decrease in crystallinity of the S5001 sample (point-ring reflexes on the SAED image of the sample S5001 on Fig.7d)

3.1.3. Textural analysis

The **Fig.9** shows the adsorption-desorption isotherms of Bi_2O_3 pure (micro and nano) and Ag-doped Bi_2O_3 (1 and 5% AgNO₃) NPs powders and their pore size distribution relationship

To establish the possible effect of the SSA and annealing of pure and Ag-doped Bi_2O_3 nanopowders on their physicochemical properties, we tested samples of NP (**Table 1**).

Results BJH analysis

Table 2 Changes in the Texture Parameters of Samples S0, S1, and S5 after Annealing in Air

Samples	SSA,	Pore Size,	Pore Volume,
	m²/g	nm	cm ³ /g
S _{target} MICRO	1.4	21.5	0.04
SO	13.2	32.4	0.11
S200	23.0	25.1	0.12
S300	10.0	31.4	0.07
S500	2.7	43.1	0.02
S750	0.45	25.4	0.01
S1	20.3	24.2	0.15
S2001	23.7	22.7	0.16
S3001	15.7	26.6	0.12
S5001	-		
S7501	Sample melted		
S5	23.0	23.6	0.10
S2005	23.7	23.4	0.12
S3005	19.6	25.2	0.10
S400	15.5	30.2	0.01
S5005	1.0	-	-
S7505	Sample melted		

The micron powder (target) had a SSA of $1.4 \text{ m}^2/\text{g}$. The nitrogen isotherms of samples S0, S1 and S5 in **(Fig. 9 c, e, g)** belong to the IV type with an H3 hysteresis loop according to UIPAC classification. The surface of the NP increased more than 16 times compared to the SSA of micron powder, the pore volume increased 2.5 times, the pore size increased slightly (~ 10%).

Doping of the Ag target caused a significant change in SSA and pore size in Ag-doped NPs compared to the NP of pure Bi_2O_3 . The SSA of Ag-doped NPs of not annealed S1 and S5 samples grew from 13.2 m²/g (sample S0) to (20.3-23.0) m²/g, respectively. In a sample of S1 with a low concentration of dopant, ~ pore volume increased 1.5 times, and the pore size of samples S1 and S5 decreased by more than 25%, regardless of the concentration of Ag in the samples.

Annealing samples S0, S1 and S5 at 200 ° C resulted in an increase in SSA in all samples as a result of evaporation of water and carbon-containing compounds from the surface of the NP. Samples S0, S1 and

S5 showed maximum SSA values after annealing in air at 200 ° C, as clearly seen in **Fig. 10**, which shows the dependence of the change in the SSA of all three samples on the air annealing temperature up to 750 °C. The SSA values of the S200, S2001 and S2005 samples were almost the same. Among annealed samples, the maximum SSA (23.7 m²/g), the minimum pore size (22.7 nm) and the maximum pore volume (0.16 m²/g) were recorded in a S2001 sample with a minimum Ag concentration.

Note that the S7501 and S7505 samples melted during annealing at a temperature of 750^oC, which is well consistent with the state diagram of the eutectic system Ag-Bi₂O₃ **[43]** where the eutectic $L \rightarrow Ag+Bi_2O_3$ conversion temperature is 687 ° C. The radius of the Ag ⁺ ion (0.115 nm) slightly exceeds the radius of the Bi³⁺ ion (0.103 nm), which contributes to the formation of a solid solution of Ag in the Bi₂O₃ lattice. However, the appearance of an additional peak on Ag-doped Bi₂O₃ NPs X-ray diffractograms clearly indicates the need to reduce the amount of AgNO₃ additive in micron powder Bi₂O₃ to produce a single-phase silver solid solution in bismuth oxide not containing excess silver. Multimodal pore size distribution in the NP Bi₂O₃pure **(Fig. 9d)** changed to unimodal distribution in silver-doped samples, with maxima of about 20-25 nm **(Fig. 9f, 9h)**. Improved texture parameters of Ag doped Bi₂O₃ NPs indicate the potential use of such NPs as nanocontainers for drug delivery, which is consistent with recent research findings **[44]**.

3.2. Thermal analysis

We have recorded synchronous DSC-TG thermograms and mass spectra of H_2O and CO_2 NP pure and Agdoped Bi_2O_3 . Analysis of heating/cooling thermograms of sample SO *in argon* was performed earlier in [19].

Thermograms of heating/cooling from the synchronous DSC-TG analysis of sample S0 *in air* atmosphere are given in **Fig.11a**. The primary heating/cooling are shown *in curves 1 and 2*, respectively, and the secondary heating/cooling are shown *in curves 3 and 4*, respectively. Mass spectra H_2O and CO_2 are given *on curves 5 and 6*. Change of sample weight is given on the thermogram TG (*curve 7*)

The phase transformations recorded *on the heating curve 1* are well consistent with the phase composition data of sample S0, which consists of an amorphous component and crystalline phases (α and β -Bi₂O₃). The primary heating and cooling curves of sample S0 are, for convenience, enlarged in **Fig.11b** and **Fig.11c**, respectively. First (**Fig. 11b**), in the range of 40-200°C, water adsorbed on the surface and in the pores of the NP evaporates from the sample -endothermic peak *1* on curve DSC. Synchronous reduction of sample weight on curve TG and the peak on water mass spectrum also confirmed the process of water evaporation in the range of 40-200°C.

At the temperature of 244°C, a exothermic peak 2 appeared on the DSC curve, caused by crystallization of the amorphous fraction in sample S0. At the temperature of 290 °C, a slight decrease in sample weight on the TG curve caused by carbon dioxide sublimation was observed synchronously, which proves the presence of a synchronous peak on the CO₂ mass spectrum curve. Further, at the temperature of about

375°C, an extended endothermic peak **3** caused by phase transformation of $\beta \rightarrow \alpha$ was observed, which is well consistent with **[45]** data about the temperature of this phase transition. The absence of any peaks on the TG curve and the mass spectra curves of CO₂ and H₂O proves that the endothermic peak refers to solid phase conversion. Further at the temperature of about 720°C on the curve DSC there is a sharp endothermic peak, which is associated with the polymorphic transformation $\alpha \rightarrow \delta$, in consistence with the data of numerous works **[46-48]**. The absence of thermal peaks on curve DSC when the sample was further heated to 800°C confirms that the sample then remained solid when heated to the above temperature.

Two exothermic peaks from the well-known polymorphic conversions $\delta \rightarrow \beta$ (668 ⁰C) and $\beta \rightarrow \alpha$ (448 ⁰C) were present on the DSC cooling thermogram **(Fig. 11c) [53-56]**.

The absence of any thermal peaks on the cooling thermogram (*curve 4*, Fig. 8a) in the temperature range 475-150°C indicates the absence of a significant number of metal droplets of Bi. Thermal peaks from the melting of Bi were observed on the heating/cooling thermograms of the DSC sample S0 [19] when it was heated in argon to the temperature 800°C (not given here), which is consistent with the data in work [49-51].

Reheating/heating of sample S0 in temperature range 150-400°C showed **(Fig. 11a)** complete absence of any thermal conversions or evaporation (sublimation) of water and CO_2 , which proves the formation of stable at room temperature α -phase of Bi_2O_3 after heating the sample S0 to 800°C in air.

Considering strongly morphological similarity of thermograms of samples S1 and S5, for brevity, the detailed thermal analysis is given below only for sample S1 (1wt % AgNO₃%).

At the first heating of sample S1 **(Fig. 12)** there were four thermal peaks on curve DSC: endothermic peak **1** from evaporation of the adsorbed water in the temperature range 40-180 °C (the peak was followed by synchronous decrease of weight (I) on curve TG and extended peak on H₂O mass spectrum in the range of temperature from 40 to 250 °C; exothermic peak **2** in the temperature range 233-327 °C from crystallization of amorphous fraction of NP. Crystallization of an amorphous phase was followed by simultaneous evaporation of crystallizational water from pores of NP and release of gaseous CO₂ in consequence of decomposition of a carbonate of bismuth, the presence of which at sample S0 is very probable.

Curve TG of primary heating showed decrease of mass of a sample - (I) and (II) synchronously on two sites in the range of temperature from 100 to ~ 320 °C, connected with simultaneous occurrence of several processes in a sample (water evaporation, removal of CO_2 at crystallization of an amorphous phase and decomposition of a carbonate of bismuth) Decomposition of a carbonate of bismuth was also confirmed by the existence of the second, small peak on H₂O mass spectrum. The exothermic peak *3*, which was present only at DSC of curves of primary heating of argentiferous samples S1 and S5 was the most interesting. Emergence of peak 3 was probably connected with availability of oxide of Ag₂O

silver in samples S0 and S5, which has a low decomposition temperature of 300 °C. Also, on curve TG of samples S1 (Fig. 12) and S5 (Fig.13), a continuous growth of weight beginning from the identical temperature of 318 °C was observed. In our opinion, increase in mass of samples was caused by oxidation of metal NPles Ag and nanoscale droplets of Bi which were present initially at samples S1 and S5. Earlier, we showed existence of clusters of Bi about 3-5 nanometers in size in NP Bi2O3 annealed in air at temperatures of 200-750 °C [19, 52, 53]. Nanoparticles (droplets) were formed in samples as a result of decomposition of a carbonate of bismuth when heating above 318 °C and due to the restoration of Ag doped Bi₂O₃ vapors of a target to metal Ag in a vacuum at PEBE. It is interesting that gain of mass of sample S0 of not doped Bi₂O₃ also began at the temperature of 318 °C, which demonstrates that a gain of weight in samples S1, S5 and S0 was caused by oxidation of droplets of Bi, but not oxidation of NPles Ag. Doping of Ag considerably affected temperatures of all, without exception, phase transitions in sample S0 (Table 3). Temperature of crystallization of the amorphous phase Tcryst in samples S1 and S5 monotonously decreased from 244 to 211°C. The specified circumstance is favorable in terms of the transition of initial multiphase sample SO (α , β , amorp) into the single-phase sample containing the most active for use in a photocatalysis, β -Bi₂O₃ phase. The amorphous phase, as we know, has adverse effect on photocatalytic properties of oxide of bismuth [54]. As it will be shown below, crystallization of amorphous components in Ag-doped Bi₂O₃ samples at the lowered temperature positively affected their main physical and chemical characteristics: catalytic activity (the samples annealed at 300 °C showed the best photocatalytic activity), textural properties (delay of reduction of SSA at annealing temperature increase was observed, see Table 3), structural parameters (doping with Ag constrained growth of the size of nanocrystals when annealing in air in comparison with growth of crystals when annealing the not doped sample of S0, see Table 1).

Table 3

Sample	T _{cryst} , °C	T _d , °C	Т _{р.t.} , °С
S0	244	no phase transition	375
S1	233	308	326
S5	211	288	348

Tcryst- Crystallization temperature of the amorphous phase

Td- decomposition temperature of Ag_2O

T p.t.- phase transition temperature of $\beta \rightarrow \alpha$

3.3. Magnetic properties of Ag-doped Bi_2O_3 NCs

Fig. 14 shows the magnetization curves of the target material (1) and the nanopowder immediately after spraying (2, 3, 4).

The diamagnetic susceptibility of initial powder Bi_2O_3 was $1.8 \ 10^{-7} \ cm^3/g$. The ferromagnetic contribution was negligible, within experimental error. The susceptibility of NPIes Bi_2O_3 received by PEBE increased, perhaps, at the expense of paramagnetic deposits of unclear nature, the existence of which was noted in monocrystals **[55]**. The ferromagnetic contribution changed signifacantly – up to 3 memu/g, which considerably exceeds an experimental error. The properties of massive monocrystals Bi_2O_3 were analyzed in **[55]**, the ferromagnetic contribution wasn't observed. Possible, emergence of ferromagnetism in oxide of bismuth is characteristic only of samples with a big SSA, such as NPs. Such features were observed for a lot of other materials **[56]**, but there is no conventional theory which would explain this phenomenon now.

Silver additives (1 and 5 wt. 3% $AgNO_3$) didn't affect susceptibility of Ag doped NP (curves 3 and 4 on **Fig.14**). Reduction of a ferromagnetic contribution which was identical to samples S1 and S5 was observed. Further studying the influence of additives of silver at concentration of Ag less than 1% is required.

3.4. Catalytic properties of Ag-doped Bi_2O_3 NPs

Results of measurement of photocatalytic properties of Ag-doped Bi_2O_3 NP are presented on **Fig.15** and **Fig.16**. Data on the photocatalytic properties of annealed not doped by NP Bi_2O_3 were provided by us earlier in **[19]**.

The dependence of discoloration of MO solution on the time of exposure to UV radiation was described by the linear equation of y=kx+b, where coefficient k is the speed of photodestruction (discoloration). The larger the value of k, the quicker the solution became colorless.

Samples of bismuth oxide S1, S5 and S3001, S3005 at concentration of 300 µg/ml showed the best photocatalytic activity among samples with identical concentration of a dopant. Speed of photodecomposition of samples is presented in **Table 4-6**.

Table 4. Value of the coefficient k for NP Bi_2O_3						
Sample	Concentration 10)0 µg/ml	Concentration 300 µg/ml			
DI ₂ O ₃	Absolute value	Lead to control	Absolute value	Lead to control		
Control	-0,0249	1	-0,0152	1		
S0	-0,0295	1,18	-0,0264	1,74		
S200	-0,0186	0,74	-0,0198	1,30		
S300	-0,0208	0,84	-0,0265	1,75		
S500	-0,0184	0,74	-0,0216	1,42		
S750	-0,0198	0,80	-0,0159	1,04		
Table 5. Value of the coefficient k for NP Bi_2O_3 + 1 wt. % AgNO ₃						
Sample	Concentration 100 µg/ml		Concentration 300 µg/ml			
	Absolute value	Lead to control	Absolute value	Lead to control		
Control	-0,0134	1	-0,0134	1		
S1	-0,0139	1,03	-0,0261	1,9		
S2001	-0,0076	0,57	-0,016	1,19		
S5001	-0,0077	0,57	-0,0086	0,64		
Table 6. Value of the coefficient k for NP Bi_2O_3 + 5 wt.% AgNO ₃						
Sample	Concentration 10)0 µg/ml	Concentration 300 µg/ml			
	Absolute value	Lead to control	Absolute value	Lead to control		
Control	-0,0148	1	-0,0146	1		
S5	-0,0246	1,66	-0,031	2,12		
S2005	-0,0178	1,20	-0,0156	1,06		
S3005	-0,0156	1,18	-0,031	2,12		
S4005	-0,0175	1,18	-0,0168	1,15		
S5005	-0,0149	1,01	-0,0126	0,86		

Earlier, we established **[19]** that the maximum photocatalytic activity among the samples of not doped Bi₂O₃ annealed in air up to the temperature of 750 of °C was also shown by samples S0 and S300.

It is necessary to identify some of the most important parameters of semiconductor powders which affect their photocatalytic activity: width of the forbidden zone, a specific surface area, the size of grains (CSR), phase structure, concentration of a dopant and some others.

From textural data (see **Table 2**) and dependences of SSA on temperature of annealing given in **Fig. 10**, we notice the lack of direct correlation between SSA and photocatalytic activity of the samples of the pure and doped with Ag bismuth oxide that showed the maximum photocatalytic activity (samples S0,S1, S5 and S300, S3001 and S3005) as the above-stated samples have wide spacing of SSA values on an absolute value and besides, the maximum activity was shown by all samples annealed at a temperature of 300 ⁰C, the SSA of which is less than SSA of initial samples (see **Fig. 10**).

The size of grains also doesn't correlate with photocatalytic activity of samples, in particular as sample S2005 that didn't show high photocatalytic activity had the minimum size of CSR (10 nm).

The correlation with phase structure of samples was also absent, as the bismuth carbonate (83.5%) was the dominating phase in not doped sample S300, and in the corresponding silver-containing phases S3001 and S3005 β -phase Bi₂O₃ dominated.

The direct correlation was observed between concentration of a dopant in not annealed samples and their speed of a photodestruction of MO which increased at increase in concentration of Ag. Also, with an increase in Ag concentration in not annealed S0, S1 and S5 samples, monotonous growth of β -phase grains was observed from 10 to 25 nm.

The lack of experimental data on the effect of doping and annealing temperature on the width of the forbidden zone did not allow us to estimate the effect of the width of the forbidden zone on their photocatalytic activity. In addition, further studies of photocatalytic activity using a radiation source in the visible range of 400-700 nm are needed, as well as studies of the morphology and surface properties of NPles, the effect of which on the PC activity of the samples is certain.

A 1.3 eV band gap Ag_2O is known to exhibit strong absorption of both UV and visible light **[57]**. Therefore, the possible presence of Ag_2O in the Ag-doped Bi_2O_3 structure can increase the visible light absorption range of the silver-containing photocatalyst **[58, 59]**. The band gap Bi_2O_3 is about 2.1 -2.82 eV **[60]** and the band gap Ag_2O -Bi₂O₃ is 2.30 **[59]**, showing an obvious decrease. Reducing the band gap of the nanocomposite (Ag_2O -Bi₂O₃) results in absorption of visible light.

In **[61]**, the photocatalytic activity of Bi_2O_3 and $Ag_2O-Bi_2O_3$ was evaluated by decomposing an aqueous solution of methyl orange (MO) as a model dye effluent. Bi_2O_3 was synthesized by chemical precipitation. Structural analysis showed that the Bi_2O_3 contained a unique well-crystallized phase and an average crystallite size of 22.4 nm. SEM analysis showed that the particle size of the Bi2O3 was generally in the

range of 16-22 nm. The most important variables affecting photocatalytic degradation of dyes, namely reaction time, initial pH and catalyst dosage, were studied and optimal amounts were found after 60 minutes, 5.58 and 0.025 g, respectively. A good correlation between experimental and predicted responses was found, confirming the reliability of the model. The inclusion of Ag_2O in the structure of the composite led to a decrease in the band gap and its response to visible light. Since a large percentage of sunlight constitutes visible light, the nanocomposite can Ag_2O -Bi₂O₃ be used as an effective visible light-controlled photocatalyst to decompose dyes under the influence of sunlight

Zhong, et al **[62]** examined the nano-spheres of bismuth oxide decorated with Ag. Silver-decorated bismuth oxide nanospheres showed superior photocatalytic activity compared to unmodified Bi_2O_3 nanospheres. When irradiated with visible light for 10. 40 and 100 minutes, Cr (VI) was completely removed from the water using Ag/Bi₂O₃ nanocomposites with Ag 2.5. 5.0 and 10% by weight, respectively. The nanospheres of Ag/Bi₂O₃ with a concentration of 2.5 wt% Ag proved very promising for water purification from heavy metals **[62]**. The results of **[62]** are consistent with our observations of a low silver concentration in the most active Ag-Bi₂O₃ photocatalysts.

3.5. PL spectra of Ag-doped Bi₂O₃ NCs

PL spectra of annealed Bi_2O_3 pure samples were described in detail in our early works **[19, 20]**. The addition of the silver affected the PL spectra of Ag doped Bi_2O_3 samples as follows: after annealing at 750 °C, the most intense peaks at wavelengths of 544 and 611 nm due to crystal defects disappeared in sample (S7501) **Fig.17a**. Apparently, the defects were annealed. In Ag doped Bi_2O_3 (5% Ag) samples, after annealing at 750 °C, peaks increased at wavelengths of 544 and 611 nm, the intensity of these peaks decreased significantly after annealing at 300 and 400 °C. However, after annealing at a temperature of 500 °C, the intensity of these peaks again increased significantly **(Fig. 17b)**. It can be assumed that an increase in the concentration of silver ions in Ag doped Bi_2O_3 (5% Ag) samples affected the formation of crystalline defects.

4. Conclusion

Using the PEBE method under vacuum (4Pa) on bismuth oxide targets supplemented with silver nitrate (1 and 5 wt.% AgNO₃), mesoporous amorphous Ag doped Bi_2O_3 NP were produced. The evolution of the various physicochemical properties of Ag doped Bi2O3 NP after their annealing in air in the temperature range of RT-750 ° C has been studied. Phase transformation of NP of annealing in air occurred according to the scheme ($\alpha + \beta + amorph$)

$$\xrightarrow{200 \ ^{0}C}_{(\beta + \operatorname{Bi}_{2}\operatorname{O}_{2}\operatorname{CO}_{2})} \xrightarrow{300 \ ^{0}C}_{(\alpha + \beta + \operatorname{Bi}_{2}\operatorname{O}_{2}\operatorname{CO}_{2})} \xrightarrow{500 \ ^{0}C}_{(\alpha)} \xrightarrow{750 \ ^{0}C}_{(\gamma + \alpha).}$$

Amorphonanocrystalline Bi and Ag drops of 3-5 nm on the surface of all annealed samples were found by HRTEM.

Silver additives (from 1 to 5% AgNO3) almost did not change the magnetic susceptibility of NP, a slight decrease in ferromagnetic contribution was observed.

The best photocatalytic activity was shown by not annealed Ag doped Bi₂O₃ samples S1 and S5 and annealed at 300 ° C S3001 and S3005 samples at a concentration of 300 µg/ml.

The disclosed synthesis method enables to obtain high-purity multiphase NPles, which by simple annealing in air at a relatively low temperature can be converted into various heterophase (single-phase) oxide powders containing inclusions of Bi and Ag drops of 3-5 nm in size. Ag (Bi) -Bi₂O₃ powders have potential applications in nanomedicine, photocatalysis and in the creation of new nanostructures containing no noble metals with a surface plasmon resonance effect.

Declarations

Declaration of Competing Interest

Authors have no conflict of interest

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Diagram of production of targets from mechanical mixtures of micron powders Bi_2O_3 and $AgNO_3$ and type of final product - Ag doped Bi_2O_3 nanopowders produced by PEBE method.



(a) X-Ray Diffraction Pattern of Bi_2O_3 (sample S0) NP prepared in vacuum; X-Ray Diffraction Patterns of Ag-doped Bi_2O_3 NPs prepared in vacuum: (b) – sample S1; (c) – sample S5, respectively.



Evolution of the phase composition of sample S0 after isothermal annealing in air (10 min) at temperatures of 200,300,500 and 750 °C.



Evolution of the phase composition of the Ag doped Bi_2O_3 sample (sample S1) after isothermal annealing (30 min) in air at temperatures of 200,300 and 500 °C.



Evolution of the phase composition of the Ag doped Bi_2O_3 sample (sample S5) after isothermal annealing (30 min) in air at temperatures of 200,300 and 50 °C.



TEM images of S0, S200,S300 and S500 samples **(a, b, c, d)**and HRTEM **((e, f, g, h)**-scale 10 nm, **(i, j, k, l)**-scale 5 nm) images of S0,S200,S300 and S500 samples, respectively. On the inserts of **a, b, c, d**images-SAED patterns.



TEM images of S0,S200,S300 samples : **(a, b, c)** -scale 50 nm **and (e, f, g)**-scale 10 nm; TEM images of S500 sample:**(d)**- scale 500 nm and **(h)**- scale 200 nm and HRTEM images of S0,S200,S300 samples: **(i,j,k)**-scale 5 nm, respectively. On the inserts of **a,b,c,d**images-SAED patterns of S0,S200,S300 and S500 samples.



TEM images of S0, S200 and S300 samples: **(a, b, c)** -scales 50 and 100 nm **and (d, e, f)**-scale 20 nm; HRTEM images of S0,S200 and S300 samples: **(g, h, i)**-scale 5 nm, respectively. On the inserts of **d, e, f** images-SAED patterns of S0, S200 and S300 samples.



Nitrogen adsorption and desorption isotherm curves (**a**,**c**,**e**) and pore size distribution (**b**,**d**,**f**) of samples Bi_2O_3 pure and Ag doped Bi_2O_3 NPs.



Dependence of SSA of pure and Ag doped $-Bi_2O_3$ samples (1 and 5% wt. Ag) on air annealing temperature.



a)Thermogram of heating/cooling of sample S0 in air in the temperature range of 40-800°C (*curves 1 and 2*, respectively); Reheating/cooling thermograms (*curves 3 and 4*, respectively) of sample S0 in temperature range 40-400 ⁰ C. Mass spectra H_2O and CO_2 -*curves 5 and 6*- respectively. The TG curve*curve 7*. b) Thermogram of heating and mass spectra H_2O and CO_2 of sample S0 in air in the temperature range of 40-800 °C c) Thermogram of cooling of sample S0 in air in the temperature range of 800-120 °C.



Thermograms of DSC-TG of heating/cooling in air and mass spectrums of H_2O and CO_2 of the sample Ag-doped Bi_2O_3 S1 (1% of AgNO₃).



Air heating DSC-TG thermograms and H_2O and CO_2 mass spectra of Ag-doped Bi_2O_3 sample S5 (5% AgNO₃).



The curves of specific magnetization of micron powder (target) – (curve 1), initial NP Bi_2O_3 (curve 2), Ag doped Bi_2O_3 NPs (curve 3)-1 wt. 3% AgNO₃, (curve 4)-5 wt. %AgNO₃ in magnetic field of 12 kOe.



(a) Kinetics of the photocatalytic degradation of MO by the Bi_2O_3+5 wt. $AgNO_3$ NPs annealed at different temperatures; (b) Linear plots of ln (C0/Ct) versus degradation time. (CONCENTRATION of 100 μ g/ml)



(a) Kinetics of the photocatalytic degradation of MO by the Bi_2O_3 + 5 wt.% AgNO₃ NPs annealed at different temperatures; (b) Linear plots of In (C0/Ct) versus degradation time. (CONCENTRATION of 300 μ g/ml).



Figure 17

PL spectra Ag doped Bi_2O_3 NPs с различной концентрацией допанта AgNO₃ (a) 1 wt.%AgNO₃ and (b) 5 wt.% AgNO₃

Supplementary Files

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