Formation of droplets in a heterophase amorphocrystalline nanopowder Bi$_2$O$_3$ produced by pulsed electron beam evaporation in vacuum

S Yu Sokovnin$^{1,2}$, V G Ilves$^2$ and A M Murzakaev$^{1,2}$

$^1$ Ural Federal University, Yekaterinburg, Russia
$^2$ Institute of Electrophysics UB RAS, Yekaterinburg, Russia

Email: sokovnin@iep.uran.ru

Abstract. In the present work, a mesoporous multiphase amorphous crystal nanopowder Bi$_2$O$_3$ with a specific surface area of up to 23 m$^2$/g was produced by pulsed electron beam evaporation in vacuum. Influence of thermal annealing (200-500 °C) of powders in air is investigated. The formation of droplets with a size of 3-5 nm on the surface of all large nanoparticles constituting the framework 3D nanopowder agglomerates was found due to extrusion of liquid bismuth from the volume during cooling.

1. Introduction
Bismuth oxide is a semiconductor that has unique optical and electrical properties and is widely used in various applications, including the production of catalysts, solid electrolytes, microelectronics, optical coatings, photocatalysis and medical applications. Synthesis of new materials under highly non-equilibrium conditions can lead to the formation of various metastable phases, which in their functional properties can significantly exceed the corresponding equilibrium phases [1].

The purpose of this work was to investigate the effect of staged thermal annealing in air atmosphere of up to 300°C of multiphase amorphous crystalline (AC) nanopowder (NP) Bi2O3 produced by pulsed electron beam evaporation (PEBE) in vacuum [2] on its morphology.

2. Experimental
The evaporation target was made on a manual press (tablet 40 * 15 mm) from bismuth oxide of the analytic grade brand (GOST 10216-80) and then annealed on air (600°C). The distance between the target and the glass substrates for collecting NP was 10-15 cm, which were heated during vapor deposition < 200°C.

Evaporation was carried out in a mode with an energy of 1.8 J in a pulse of 100 μs, at a pulse repetition rate of 50 pps for up to 45 minutes at a pressure of ~ 4 Pa. The initial NP (sample S0) was then annealed in alund crucibles at 200 and 300°C, further referred to as samples S200 and S300. The isothermal holding time is 10 minutes, cooling was carried out together with the furnace to 100-150°C. Textural properties of NP were studied by the BET method on the Micromeritics TriStar 3000 V6.03 A analyzer. The morphology and phase structure of samples were studied on the translucent electronic microscope JEM-2100.
3. Results and discussion

The results of the texture analysis are shown in table 1, which shows that the specific surface area (SSA) and pore volume of the original NP S0 varies non-monotonically from the annealing temperature. The sharp growth of the SSA of sample S200 was caused by evaporation of water from the developed surface and increased dispersion due to the crystallization of the amorphous fraction, which is also indicated by a decrease in size and an increase in pore volume. The observed marked decrease in SSA for the sample S300 probably due to sintering of the smallest nanoparticles during annealing.

Figure 1a shows agglomerates from AC nanoparticles Bi$_2$O$_3$ irregular shape (size ~ 3-10 nm) typical for the sample S0, which have a significant morphological resemblance to oxides and fluorides obtained earlier by the PEBE method [3].

| Sample | Pore size, nm | SSA, m$^2$/g | Pore volume, cm$^3$/g |
|--------|---------------|--------------|------------------------|
| Target | -             | 1.4          | -                      |
| S0     | 32.5          | 13.2         | 0.107                  |
| S200   | 25.1          | 23.0         | 0.121                  |
| S300   | 31.4          | 10.0         | 0.069                  |

Figure 1. TEM picture of the sample S0.
Blurred diffraction rings and point reflexes on the diffractogram shown in the insert confirm this. The nanoparticles hexagonal shape with perfect cut (~8 nm) was isolated on figure 1b. Its interplane distances (MPR = 0.327 nm) correspond to the cubic phase of Bi$_2$O$_3$ (or the rhombohedral phase of Bi). On figure 1c are shown amorphous regions containing individual crystalline nanoparticles, shown as MPR corresponding to the monoclinic phase Bi$_2$O$_3$ and the hexagonal phase Bi. These data confirm the multiphase composition of sample S0. At the same time, on the surface of the spherical AC nanoparticles (isolated by a white rectangle, ~8 nm), there are many hemispherical nanoparticles sizes less than 2 nm, both amorphous and crystalline, in which separate columns of atoms were viewed. On figure 1d, the cubic structure of the hardened ("frozen") is clearly visible during the growth of nanoparticle during its crystallization on a cold glass substrate, with a highly defective structure. MPR allow to attribute these nanoparticles to metallic Bi (or Bi$_2$O$_3$).

The results of microscopic analysis of annealed samples Bi$_2$O$_3$ showed (figure 2) that the nanoparticles surface (including internal cavities) in all samples turned out to be covered with quasi-spherical AC nanoparticles of close size (~2-5 nm), which can be considered as quantum dots or bismuth droplets [4]. On the sample S300 (figure 2c), a spatial framework of large nanoparticles is clearly visible, decorated with many small nanoparticles (<5 nm) located on both external and internal (figure 2d) surfaces.

Figure 2. TEM picture of the sample S200 (a), (b) and S300 (c), (d).
It can be assumed that the mechanism of droplet formation is associated with an abnormal, non-monotonic change in bismuth density after its transition to a liquid state. It is known that the volume of bismuth after melting decreases due to an increase in its density [5], which creates the prerequisites for extrusion of liquid bismuth through the oxide shell into the core-shell structures constituting the framework 3D NP agglomerates, when cooling the core-shell nanoparticles.

The oxide shell has a significantly higher melting point, so during the crystallization of the liquid bismuth enclosed in the oxide shell, the shell breaks due to its increase in volume and the liquid bismuth is extruded and solidified on the nanoparticles surface. It is natural to assume that strength, thickness, porosity, continuity also play an important role in the process of extrusion of droplets onto the nanoparticles surface. Various crystal defects in nanoparticles clusters also contribute to enhanced extrusion. Crystallization of amorphous fraction happens at a temperature up to 300°C therefore concentration of liquid Bi in structure of sample S200 is less, than in sample S300 in which in liquid state there are all droplets of bismuth, without exception. Therefore, when the samples are cooled, the number of droplets extruded onto the surface is greater in sample S300 (figure 2c).

4. Conclusions
Thus, the PEBE method produces high purity multiphase HPs which, by simple annealing on air at a relatively low temperature, can be transformed into various heterophase oxide powders containing 2-5 nm size Bi droplets on the surface of 3D oxide nanostructures. Powders Bi- Bi₂O₃ have the prospect of use in nanomedicine, photocatalysis and in the creation of new nanostructures that do not contain noble metals, with the effect of surface plasmon resonance.

Acknowledgements
The study was carried out with the financial support of RFFI and the Czech Science Foundation as part of scientific project No. 20-58-26002.

References
[1] Esposito V and Castelli I E 2020 Adv. Mater. Interfaces. 7 1902090
[2] Sokovnin S Y, Ilves V G and Zuev M G 2016 Engineering of Nanobiomaterials: Applications of Nanobiomaterials vol 2 ed A Grumezescu (Amsterdam: Elsevier) pp 29–75
[3] Il'ves V G and Sokovnin S Yu 2011 Nanotechnologies in Russia 6 137–43
[4] Kumari L, Lin J H and Ma1 Y R 2007 Nanotechnology 18 295605
[5] Geng H, Sun C, Wang R, Qi X G and Zhang N 2007 Chinese Sci. Bull. 52 2031