

# Nanostructured Bismuth Oxide

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We overviewed the complex chemical behavior of bismuth during the transformation of its compounds to oxide and bismuth oxide phase transitions.

bismuth oxide

nanoparticle

bismuth oxynitrate

bismuth oxychloride

## 1. Introduction

Nanosized oxides and related materials have raised more and more interest in the scientific community due to their cost-effective fabrication processes [1][2], high stability [3] and versatility in terms of morphology [4][5]. Furthermore, the high atomic number of bismuth brings about a high energy radiation attenuation larger than that of lead at an almost negligible risk of toxicity [6]. The combinations of bismuth properties represent a unique chance to exploit singularly or simultaneously cytotoxicity and diagnostic effects.

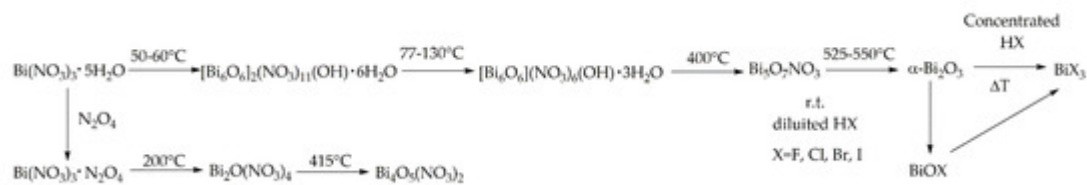
## 2. Bismuth Oxide and Related Materials: Productive Strategies

Nowadays, bismuth is mainly produced as a side product of lead streams and could be isolated through the Betterton–Kroll process [7] or through an electrochemical procedure known as Betts electrolytic process [8]. It is obtained in a highly purified form for those applications where it is used as a replacement for lead.

Commonly, bismuth is used in form of halide, oxo-halide, nitrate and oxides derivatives. Bismuth halides ( $\text{BiX}_3$ , X = F, Cl, Br, I) are generally prepared by treating bismuth oxide in a watery medium by adding the specific HX acid. Bismuth trihalides are bipyramidal molecular species in the gas phase with angle X-Bi-X in the range 96–100° [9]. In the solid phase, they show a variety of different structures based on the halogen present in the crystals.  $\text{BiF}_3$  shows a pseudo-ionic structure with tricapped trigonal prismatic motive where bismuth atoms are surrounded by nine fluoride atoms, while the other halides show bicapped trigonal prism crystals. Bismuth oxide halides ( $\text{BiOX}$ ) are formed by partial hydrolysis of bismuth halides.  $\text{BiOF}$  and  $\text{BiOI}$  can also be made by heating the corresponding halides in the air.  $\text{BiOX}$  have complex layer lattice structures [10] and, when heated up to 600 °C,  $\text{BiOCl}$  or  $\text{BiOBr}$  are decomposed by forming  $\text{Bi}_{24}\text{O}_{31}\text{X}_{10}$  [11].

Moving on, bismuth can easily be produced as bismuth nitrate. Firstly, it is recovered as  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  through crystallization after hydrolysis of  $\text{Bi}_2\text{O}_3$  by using concentrated nitric acid. If a diluted acid is used is possible to recover the basic salt  $\text{BiO}(\text{NO}_3)$ .  $\text{BiO}(\text{NO}_3)$  could be also produced by precipitation treating  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  at 150

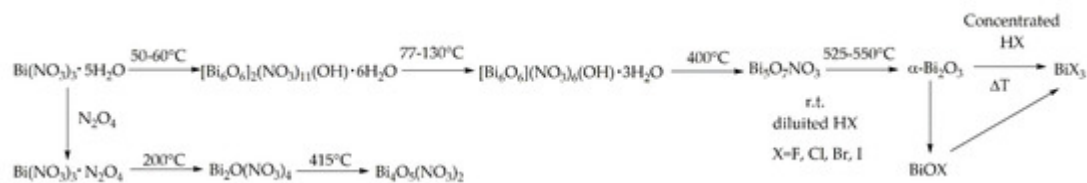
°C with butanol forming road-like structures as reported by Liu et al. [12]. As clearly enlighten by Briand and Burford [13] the hydrolysis of  $\text{Bi}(\text{NO}_3)_3 \times 5\text{H}_2\text{O}$  could lead to a plethora of different compounds. Furthermore, several attempts were reported in the literature [14][15][16][17][18] pursuing the thermal oxodehydration of  $\text{Bi}(\text{NO}_3)_3 \times 5\text{H}_2\text{O}$  with the formation of a series of complex species as summarized in Figure 1.



**Figure 1.** Comprehensive scheme of chemical evolution of  $\text{Bi}(\text{NO}_3)_3 \times 5 \text{H}_2\text{O}$ .

An interesting study was reported by Tanveer et al. [4] about the transition from  $\text{Bi}(\text{NO}_3)_3 \times 5\text{H}_2\text{O}$  to  $\text{Bi}_5\text{O}_7\text{NO}_3$  showing how it is possible to isolate a species of  $\text{Bi}_5\text{O}_7\text{NO}_3$  tailored on the surface with  $\beta\text{-Bi}_2\text{O}_3$ .

Bismuth oxides are the other deeply studied class of bismuth compounds and they present four different phases [19] as reported in Figure 2.



**Figure 2.** Scheme of phase transition of bismuth oxide.

At room temperature, monoclinic  $\alpha\text{-Bi}_2\text{O}_3$  is the common stable phase with a polymeric-distorted layered structure composed of pentacoordinate bismuth atoms enclosed into pseudo-octahedral units. At a temperature higher than 710 °C,  $\alpha$  phase is converted into the cubic  $\delta$  phase that has a defective structure with random oxygen vacancies [20]. The  $\beta$  phase and several oxygen-rich forms are closely related to the  $\delta$  phase. In particular, the vacancy structures of highly defected bismuth oxides some sites filled with  $\text{O}^{2-}$  together with Bi(III) and Bi (V) sites. Bismuth oxide  $\gamma$ -phase shows also a cubic structure but it is highly unstable and hard to synthesize without supporting it onto other oxides or metallic species [21]. The other two polymorphic metastable bismuth oxide phases are known as the  $\omega$  phase stable at temperatures higher than 800 °C [22] and the  $\epsilon$  phase isolated in 2006 by Cornei and co-workers [23].

Bismuth(V) oxides are less stable than Bi(III) but several studies reported their preparation as lithium [24] or sodium [25] salt derivatives.

Bismuth derivatives were also studied for the production of colloidal phases. Kiran et al. [26] synthesized a bismuth-substituted cobalt ferrite with a nominal formula  $\text{CoFe}_2\text{-}0.1\text{Bi}_{0.1}\text{O}_4$  quite active for the reduction of 4-nitrophenol to 4-aminophenol in a watery solution of sodium borhydride. Metal bismuth nanoparticles were produced by Petsom

et al.<sup>[27]</sup> showing that the size of the nanoparticles can be tuned by adding different amounts of ionic and non-ionic surfactants.

Furthermore, several organometallic species of bismuth such as subgallate <sup>[28]</sup> and subsalicylate<sup>[29]</sup> have found use in medical applications that will be more thoroughly discussed in the next sections and briefly summarized in Table 1.

**Table 1.** Summary of main properties of bismuth and related compounds.

Bismuth Species	Advantages	Issues
Metallic bismuth	<ul style="list-style-type: none"> <li>§ Easy to synthesized</li> <li>§ High size control</li> <li>§ Highest concentration of radiopaque atoms</li> </ul>	<ul style="list-style-type: none"> <li>§ High cytotoxicity for low average size particles</li> <li>§ Only spherical shaped</li> <li>§ Neat surfaces without any functional groups</li> </ul>
Organometallic bismuth	<ul style="list-style-type: none"> <li>§ Hydrosoluble</li> <li>§ High cellular uptake</li> <li>§ High stability</li> </ul>	<ul style="list-style-type: none"> <li>§ Low concentration of radiopaque atoms</li> <li>§ Fast excretion</li> <li>§ Could trespass the hematoencephalic barrier<sup>[30]</sup></li> </ul>
Bismuth nitrates	<ul style="list-style-type: none"> <li>§ High shape tunability</li> <li>§ Highly tailoring surface</li> </ul>	<ul style="list-style-type: none"> <li>§ Fast hydrolysis in watery phase under mild conditions</li> <li>§ Difficult to isolated as pure compounds</li> <li>§ Difficult to predict the correct active species</li> </ul>
Bismuth halide and oxohalides	<ul style="list-style-type: none"> <li>§ Easily synthesizable</li> <li>§ Photocatalytic activity</li> </ul>	<ul style="list-style-type: none"> <li>§ Oxidizable</li> <li>§ Hygroscopic</li> </ul>

	§ Highly acidic	
Bismuth oxides	§ Highly stable	
	§ Easy to synthesized	
	§ High size control	§ Highly hydrophobic
	§ Poor cytotoxicity	§ Phase impurities
	§ Good cellular uptake	§ Surface defects
	§ Photocatalytic activity	

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