Investigations on Self-Organization of Bismuth Oxido Clusters - Precursors and Model Compounds for Metastable Bismuth Oxides

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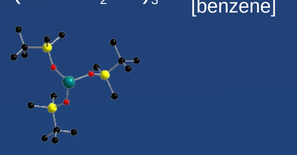
Introduction

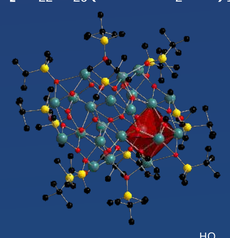
Bismuth oxides are interesting materials in terms of their environmentally benign, non-toxic behavior and their flexible usage.[1] For example α-Bi_2O_3/Bi_2O_4 nanocomposites are excellent photocatalysts and δ-Bi_2O_3 exhibits high oxide ionic conductivity.[2-4] However, targeted synthesis of polymorphs of bismuth(III) oxides is difficult. Six different polymorphs are known until now. α-Bi_2O_3 with its monoclinic structure is stable at room temperature. Upon heating it is transformed into the cubic δ phase at approximately 730 °C which is stable up to its melting point. On cooling one out of two metastable bismuth(III) oxides, tetragonal β- or cubic γ-Bi_2O_3, is stabilized depending on the reaction conditions. So far factors that control polymorphism in bismuth(III) oxides are not fully understood. In our approach we use nanoscaled bismuth oxido clusters[5,6] as model compounds and starting materials for the synthesis of bismuth(III) oxide polymorphs. The clusters show an interesting structural relationship with δ- and β-Bi_2O_3.

Here we present the synthesis, characterization and reactivity of several bismuth oxido clusters. The investigations are supported by in-situ X-ray powder diffraction, single crystal X-ray diffraction analysis, electrospray mass spectrometry experiments and molecular dynamic simulations which provide insight into the nucleation and decomposition process of bismuth oxido clusters to give bismuth oxides.

Synthesis of Bismuth Oxido Clusters

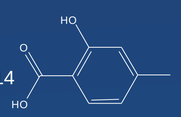
$Bi(OSiMe_2{}^tBu)_3$ —moisture, [benzene]→ $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$



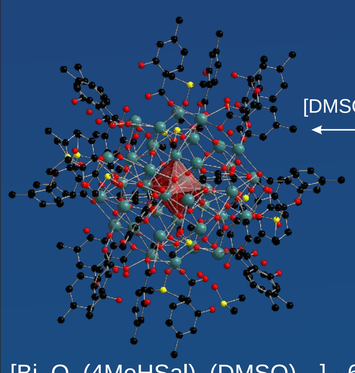


triclinic, P-1
a = 20.7120(7) Å a = 100.705(3)°
b = 20.9111(7) Å b = 114.099(3)°
c = 22.1887(8) Å g = 107.957(3)°
V = 7789.3(5) Å^3
R1 = 0.0532, wR2 = 0.0925

- 14 $Me_2{}^tBuSiOH$ [THF] + 14 „4MeH$_2$Sal“



[DMSO] ← „$[Bi_{22}O_{26}(4MeHSal)_{14}]$“ amorphous powder
EA: C 19.4 % (ber. 18.9 %)
H 1.7 % (ber. 1.4 %)
ESI-MS (see below)



$[Bi_{38}O_{45}(4MeHSal)_{24}(DMSO)_{13.2}] \cdot 6\ H_2O$

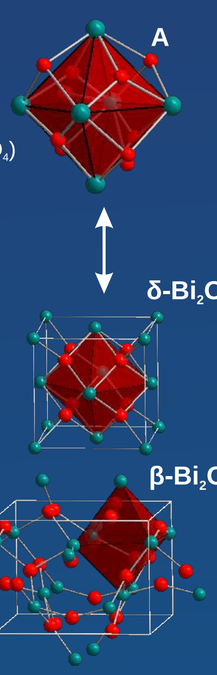
Stability of the cluster in the gas phase?

Bismuth Oxido Clusters - good Precursors for the Synthesis of Metastable Bismuth Oxides?

*number (z) of the „Bi_6-octahedron“ **A** in structural characterized bismuth oxido clusters*

z	
1	$[Bi_4O_2(OSiEt_3)_8]$
	$[Bi_6O_{4+y}(OH_{4-y})]^{(6-y)}X_{(8-y)}$ X = NO_3, Otf, ClO_4)
	$[Bi_9O_7(OSiMe_3)_{13}]$
4	$[Bi_{18}O_{18}(OSiMe_3)_{18}]$
	$[Bi_{20}O_{18}(OSiMe_3)_{24}]$
8	$[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$
10	$[Bi_{33}NaO_{38}(OSiMe_3)_{24}]$
13	$[Bi_{38}O_{45}(OTf)_{24}]$, $[Bi_{38}O_{45}(hfac)_{24}]$
	$[Bi_{38}O_{44}(HSal)_{26}]$, $[Bi_{38}O_{45}(HSal)_{22}(OH)_2]$
20	$[Bi_{50}Na_2O_{64}(OH)_2(OSiMe_3)_{22}]$
∞	Bi_2O_3

- The „Bi_6-octahedron“, found in all bismuth oxido clusters, is part of the structures of tetragonal b- and cubic d-Bi_2O_3.



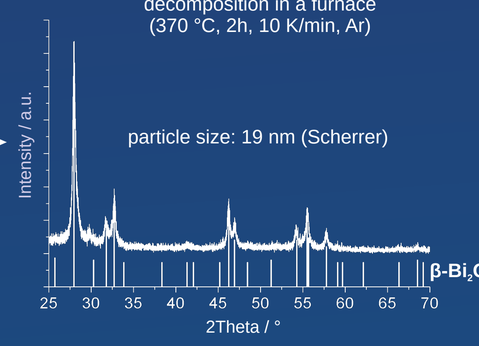
Hydrolysis of Bismuth Oxido Clusters

$[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$ —[THF], + H_2O, - $Me_2{}^tBuSiOH$→ „$[Bi_{22}O_{26}(OH)_{14}]$“ —heating→

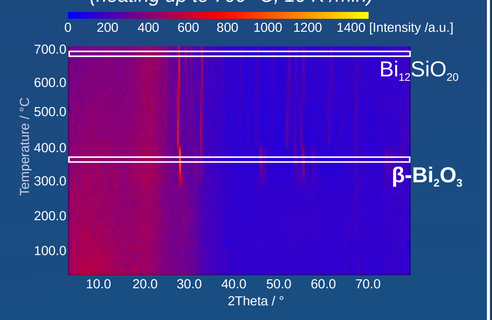
EDX of amorphous powder:
found Bi 89.9 %, O 10.1 %, Si 0.0 %
calc. Bi 87.6 %, O 12.9 %

in-situ PXRD in a quartz glas capillary

ex-situ PXRD after decomposition in a furnace (370 °C, 2h, 10 K/min, Ar)



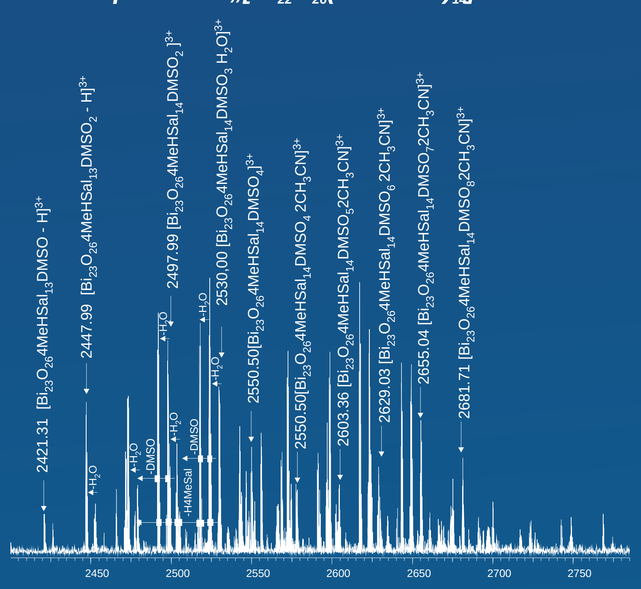
temperature dependent PXRD (heating up to 700 °C; 10 K /min)



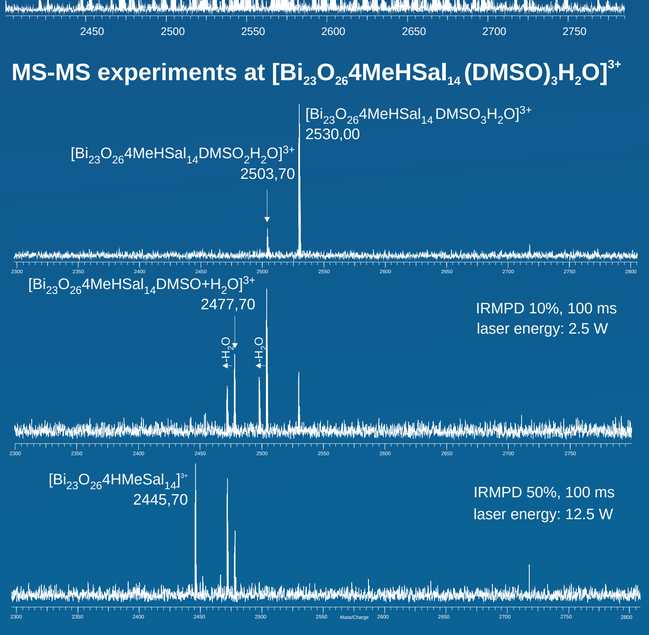
- *in-situ* PXRD experiments show the formation of β-Bi_2O_3 in the range of 300 °C to 400 °C; higher temperatures result in the formation of $Bi_{12}SiO_{20}$, which is a result of the contact with the quartz glas capillary
- heating to 370 °C in a furnace under argon results in the formation of nanoscaled β-Bi_2O_3
- as prepared β-Bi_2O_3 is stable up to 470 °C

ESI-MS of Bismuth Oxido Clusters

ESI-MS spectra of „$[Bi_{22}O_{26}(4MeHSal)_{14}]$“

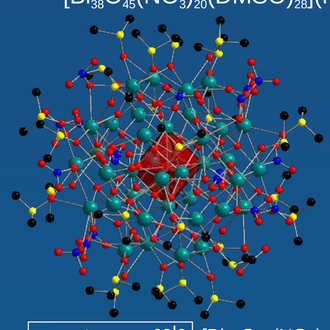


MS-MS experiments at $[Bi_{23}O_{26}4MeHSal_{14}(DMSO)_3H_2O]^{3+}$

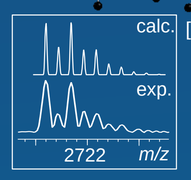


Nucleation Studies and Molecular Dynamic Simulations

$[Bi_{38}O_{45}(NO_3)_{20}(DMSO)_{28}](NO_3)_4(DMSO)_4$

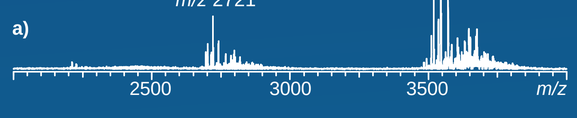


cluster consists of 12 $[Bi_6O_8]$-units and a $[Bi_6O_9]$-unit in the center of the cluster

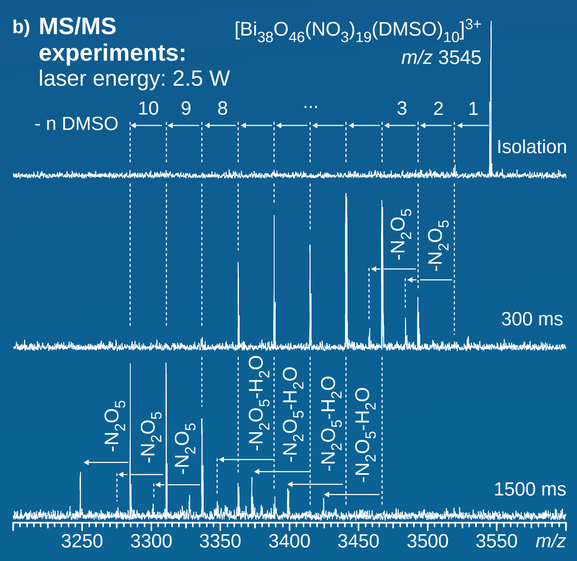


$[Bi_{38}O_{46}(NO_3)_{19}(DMSO)_{10}]^{3+}$ *m/z* 3545

$[Bi_{38}O_{46}(NO_3)_{18}(DMSO)_{14}]^{4+}$ *m/z* 2721



b) MS/MS experiments:
laser energy: 2.5 W



$[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ (x,y=0) —1. DMSO / HNO_3 2. acetone→

$Bi(NO_3)_3{\cdot}5H_2O$ (x=2 y=3.5) —DMSO, additive: sodium methacrylate→

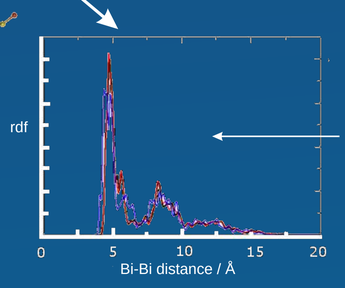
$[Bi_{38}O_{45}(NO_3)_{20+x}(DMSO)_{28-x}](NO_3)_{4-x}(DMSO)_{4-y}$

ESI-MS investigations (x,y=0)

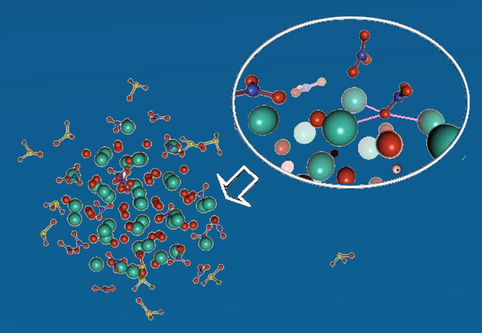
results ESI-MS:
- high stability of the $\{Bi_{38}O_{46}\}$ cluster core
- core fragmentation occurs after complete desolvation

results MS/MS:
- dissociation of all DMSO molecules
- formation of N_2O_5 and O^{2-} from two molecules of NO_3^-
- formation of ligand free („desolvated“) $\{Bi_{38}O_{57}\}$ clusters possible

molecular dynamic simulations starting from $[Bi_{38}O_{47}(NO_3)_{20}(DMSO)_{26}]$ (x,y=0)



radial distribution functions of $[Bi_{38}O_{47}(NO_3)_{20}(DMSO)_{26}]$ (black), $[Bi_{38}O_{47}(NO_3)_{20}]$ (red) & $[Bi_{38}O_{47}]$ (blue)



favorable molecular structure for formation and dissociation of N_2O_5 found

Information from Molecular Dynamic Simulations:
- cluster stability in the gas phase
- influence of ligands towards structural evolution and dissociation properties of the clusters

results molecular dynamic simulations:
- above 500 K: evaporation of DMSO molecules on a nanosecond scale
- inner structure of the cluster is only marginally affected even by full DMSO dissociation
- even at temperatures of 1000 K no nitrate ion dissociation observed
- favorable molecular arrangements for dissociation of N_2O_5 found (see highlighted area)
- if dissociation of N_2O_5 is assumed, the neutral $Bi_{38}O_{57}$ was found as a stable moiety (but structural motifs are rearranged drastically; see radial distribution functions)

Conclusion

- **decomposition** of fully hydrolyzed Bi_{22}-silanolate clusters lead to formation of **nanoscaled β-Bi_2O_3**
- **high stability of bismuth oxido clusters**, even in the gas phase; formation of „desolvated“ clusters possible
- crystallization of functionalized Bi_{22}-clusters from DMSO lead to the **formation of Bi_{38}-oxido clusters**
- **molecular dynamic simulations** support the loss of all DMSO molecules in the gas phase and the **formation of $\{Bi_{38}O_{57}\}$ as stable moiety**

References

[1] M. Mehring, *Coord. Chem. Rev.* **2007**, *251*, 974. [2] A. Hameed, T. Montini, V. Gombac, P. Fornasiero, *J. Am. Chem. Soc.* **2008**, *130*, 9658. [3] R. Punn, A. M. Feteira, D. C. Sinclair, C. Greaves, *J. Am. Chem. Soc.* **2006**, *128*, 15386. [4] P. Shuk, H. D. Wiemhofer, U. Guth, W. Gopel, M. Greenblatt, *Solid State Ionics* **1996**, *89*, 179. [5] L. Miersch, M. Schlesinger, R. W. Troff, C. A. Schalley, T. Rüffer, H. Lang, D. Zahn, M. Mehring, *Chem. Eur. J.* **2011**, *17*, 6985. [6] L. Miersch, T. Rüffer, H. Lang, S. Schulze, M. Hietschold, D. Zahn, M. Mehring, *Eur. J. Inorg. Chem.* **2010**, 4763.

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