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# *In Situ* Growth of Bi Nanoparticles on $NaBiO_3$, δ-, and β-$Bi_2O_3$ Surfaces: Electron Irradiation and Theoretical Insights

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**ABSTRACT:** Herein, we present a combined experimental and theoretical study of the *in situ* growth of Bi nanoparticles on $NaBiO_3$, δ-, and β-$Bi_2O_3$ surfaces mediated by the electron beam of a high-resolution transmission electron microscope. Density functional theory and quantum theory of atoms in molecules calculations were used to gain a deeper insight into the experimental observations and to provide an atomistic basis for understanding the formation mechanism of Bi NPs on $NaBiO_3$, δ-, and β-$Bi_2O_3$ under electron beam irradiation. Analysis of the experimental data and electron density distributions suggests that the formation of Bi NPs can be related to the structural and electronic changes occurring within the octahedral [$BiO_6$] clusters, and to a lesser extent, [$NaO_6$] clusters, which serve as the constituent building blocks of $NaBiO_3$. Our findings indicate that as a function of the number of added electrons, the formation of β-$Bi_2O_3$ takes place first followed by the subsequent appearance of metallic Bi NPs generated in the crystal by electron beam irradiation.

## 1. Introduction

The properties derived from the interactions of electrons/waves with matter are of great importance in modern science and engineering. Electron beam irradiation is a necessary and promising area of research because of its wide usage and unique advantages. Furthermore, it is known to be an effective technique for changing or modifying materials; the scattered electrons exiting the back surface of the specimen are a rich source of information about the microstructure and electronic structure of the sample, which can be analyzed based on a variety of electron-solid interaction mechanisms[1-3]

Conventional techniques for characterizing the microstructure of nanomaterials rely heavily on electron microscopy techniques, in which high-energy electrons are transmited trough the specimen and provide useful information at the nanometer and sub-nanometer levels based on a variety of electron-solid interactions.[4] The electron beam generated within a transmission electron microscope (TEM) or field emission-TEM (FE-TEM) interacts with the sample during imaging and is also a very powerful tool for the fabrication and manipulation of nanostructures with the advantage of precise control at the nanoscale or single nanoparticle (NP) level.[5-6] This is because in a vacuum chamber, despite recent developments in liquid-cell and *in situ* electron microscopy, the high-energy beam used in an electron microscope is unaffected by chemicals in the surrounding environment, such as solvents, reactants, and electrolytes, which can play an essential role in regulating the chemical activity.[7-9] TEM can be used to fabricate unique highly dispersed nanomaterials by electron beam irradiation, and Bohler et al.[10] reviewed how low-energy electron irradiation is capable of initiating the synthesis of NPs and modifying surfaces with metal NPs. Very recently, Rümmeli et al.[1] reviewed the body of work available on electron-beam-induced synthesis techniques with *in situ* capabilities.

A tremendous amount of research effort has been devoted to the synthesis of metal NPs on the surfaces of different substrates as they may possess innovative properties and hold great promise for future technology.[11-12] In particular, arrays of metal NPs deposited on surfaces offer great potential for the design of novel nanomaterials for applications in areas such as catalysis, electronic nanodevices, information storage, and quantum computers.[13-18] Thus, it is crucial to investigate the mechanisms governing the formation and modification of metal NPs during characterization under electron beam irradiation.

Our research group have proven that through electron beam irradiation under Ag-based oxides such as α-$Ag_2WO_4$,[19-27] β-$Ag_2WO_4$,[28-29] $Ag_2CrO_4$,[30] $Ag_2MoO_4$,[31] β-$AgVO_3$,[32] $Ag_3PO_4$,[33] Ag NPs can be obtained on the surface of these materials. Other metal nanoparticles were also obtained with electron beam irradiation, such as Li,[34] Cu,[35] Co[36] and Au,[37] being their formation dependent on the electron beam acceleration voltage, the irradiation time, the nature of the material to be irradiated, among other factors. Even very recently, we have shown the formation and coexistence of different crystallographic phases (rhombohedral, monoclinic, and cubic) of Bi NPs synthesized by femtosecond radiation in air.[38] As a continuation of these works, in the current investigation, we demonstrate that an electron beam can be used for the formation of Bi NPs on the surface of $NaBiO_3$.

Previously, Yacaman et al.[39] reported the formation of metallic Bi NPs by focusing a TEM electron beam over $NaBiO_3$. Very recently, Zhang et al.[40] observed the formation of Bi NPs by electron irradiation of $NaBi(MoO_4)_2$ nanosheets at observable conditions (200 kV) in a TEM. While Li et al.[41] managed to unravel the *in situ* atomic-scale mechanism of crystal nucleation and growth of Bi NPs under an electron beam inside an aberration-corrected transmission electron microscope. Electrons interact with solids at the quantum level, and

improving our understanding and predicting the response of a material to the passage of electrons is critical for various applications, but remains a challenging problem. Several questions remain regarding the structural evolution of the crystal lattice during electron irradiation. Bi NPs were also produced by Bi metallic targets in solvents through laser ablation, obtaining spherical nanoparticles of rhombohedral Bi with size range between 60 to 5 nm, the size being dependent on the aperture of the laser spot size, the wavelength and laser power, pulse numbers, time slot, solvent employed, among other factors.[42-44]

In order to reproduce the experimental scenario as closely as possible, density functional theory (DFT) calculations using the quantum theory of atoms in molecules (QTAIM) were carried out to gain atomistic insights into the *in situ* growth, and structural and electronic evolution of Bi NPs in the $NaBiO_3$ crystal, as defined by the changes in the electron density. Experimental techniques such as high-resolution transmission electron microscopy (HR-TEM) were used. Energy-dispersive X-ray spectroscopy (EDS) was also employed. The results provide a valuable probe into the relationship between atomic-scale structural and electronic perturbations.

Our manuscript is organized as follows: The employed experimental techniques and theoretical methods used to model the bulk systems are described and then, the results are presented and discussed, and we finally conclude with our main findings and implications for future work.

## 2. Methods

### 2.1. Experimental procedures

Sodium bismuthate ($NaBiO_3$, 80%, Neon) with a δ-$Bi_2O_3$ impurity (see in the supporting information, Figure S1) and bismuth (III) oxide (β-$Bi_2O_3$, 99.999%, Sigma

Aldrich), both commercial reagents, were used for the experiments. A Jem-2100 LaB6 (Jeol) high resolution transmission electron microscope (HR-TEM) with an accelerating voltage of 200 kV coupled with an INCA Energy TEM 200 (Oxford) energy dispersive X-ray spectrometer (EDS) was used to irradiate the sample with electrons after depositing small amounts of the powders directly onto carbon-coated Cu grids, while pellets were prepared by ultrasonic dispersion. In addition, we used the same equipment for performing TEM and microanalysis measurements in order to characterize the structural changes of the samples. The mesh size of TEM grids is 300.

### 2.2. Theoretical methods

First-principles total energy calculations were carried out within the periodic DFT framework using the VASP program.[45] The Kohn-Sham equations were solved by means of the Perdew, Burke, and Ernzerhof exchange-correlation functional, and the electron-ion interaction described by the projector-augmented-wave pseudopotentials.[46-47] Because of the well-known limitations of standard DFT in describing the electronic structures of "strongly-correlated" compounds, a correction to the PBE wave function was made (PBE+U) by including a repulsive on-site Coulomb interaction, U, according to the formula of Dudarev et al.[48] The orbital dependence of the Coulomb and exchange interactions has been taken into account with this scheme, using a value of 6 eV for the Hubbard parameter for Bi (previously tested). The plane-wave expansion was truncated at a cut-off energy of 520 eV and the Brillouin zones were sampled through Monkhorst-Pack special k- point grids that ensured geometrical and energetic convergence for the $NaBiO_3$, β-$Bi_2O_3$, and δ-$Bi_2O_3$ structures considered in this work. In the calculations, electrons were introduced one by one up to eight in the unit cell (keyword NELECT) and the distribution of these extra electrons takes place

by means of a simultaneous geometry optimization on both the lattice parameters and the atomic positions. The relationship between charge density topology and elements of molecular structure and bonding was noted by Bader.[49] This relationship, Bader's QTAIM theory,[50-51] is now a well-recognized tool for analyzing electron density, describing interatomic interactions, and rationalizing chemical bonding, as used in previous works.[23, 26, 28, 30, 32-33, 52-53]

## 3. Results and discussion

The unit cell of $NaBiO_3$ in the ilmenite structure belongs to the space group R-3. The optimized lattice constants are a = b = 5.508 Å, c = 15.818 Å, α = β = 90°, and γ = 120°, according to other theoretical and experimental works.[54-55] There is one type of Na and one type of Bi in a $NaBiO_3$ crystal, forming both distorted octahedral clusters (see the supporting information file, Figure S2). Both [$NaO_6$] and [$BiO_6$] octahedral clusters are distorted with two different bond lengths, where the Na–O bond lengths are longer than the Bi-O bond lengths. Two phases of bismuth oxide ($Bi_2O_3$) were modeled, β-$Bi_2O_3$ and δ-$Bi_2O_3$ polymorphs. β-$Bi_2O_3$ presents a tetragonal structure belonging to the space group P42c (ICSD 62979) and δ-$Bi_2O_3$ has a cubic structure belonging to the space group $Fm\bar{3}m$, which was modeled taking into account an occupancy factor of only 0.75 in the 8c Wyckoff positions for the O atoms (ICSD 27458).

$NaBiO_3$ was characterized by X-ray diffraction (XRD) and the corresponding patterns are associated with a hexagonal structure with two hydration molecules ($NaBiO_3.2H_2O$), as described by PDF 30-1161[56] in the Joint Committee on Powder Diffraction Standards (JCPDS) database (see supporting information, Figure S1). $NaBiO_3$ crystals have a hexagonal structure belonging to the space group P3 with two molecular formula units per

unit cell (Z=2).Due to its low purity (80%), the δ-$Bi_2O_3$ phase was also present, according to PDF 52-1007[57] in the JCPDS database. These results can be attributed to the fact that $NaBiO_3.2H_2O$ is obtained at high temperatures through the oxidation of $Bi(NO_3)_3.5H_2O$ by NaOH,[58] and therefore, the hexagonal polymorph of $NaBiO_3$ and cubic polymorph of δ-$Bi_2O_3$ are obtained.

$NaBiO_3$ was irradiated using an electron beam under high *vacuum* in a TEM at 200 kV. Figure 1 shows low-magnification TEM images of the material before being irradiated. According to Figure 1B, after 10 minutes of irradiation with the electron beam, the formation of nanocrystals of Bi could be observed on the surface of the sample.

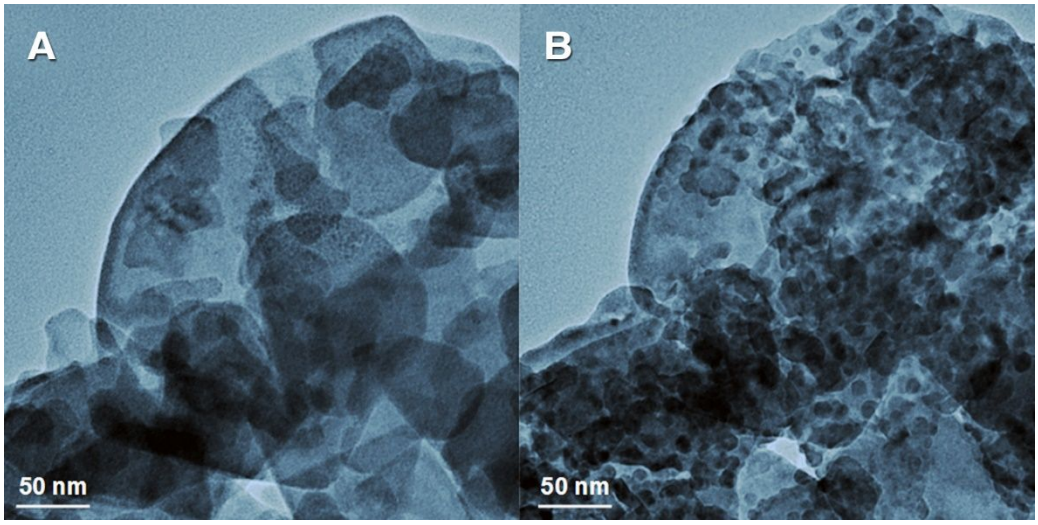


**Figure 1:** (A) Low-magnification TEM image of the sample before the irradiation by electron beam and (B) after 10 minutes of exposure to irradiation by electron beam.

The effect of exposure time was investigated and the TEM images are displayed in Figures 2A-B and 2D-E. An analysis of the results suggests that the morphology of the Bi

NPs changes with time with the formation of agglomerates with non-regular shapes and diameters of about 10-100 nm. In Figure 1B it is also possible to observe spheroidal NPs and some particles with morphology of beans or earthworms, like in figure 2A, which could be associated to the irregular shape of the initial particles or coalescence of some spheroidal NPs as an effect of electron beam irradiation. It can be observed that as the electron irradiation time increases, the Bi NPs perform a coalescence process to form larger particles. At short times of electron irradiation, the formation of NPs of Bi is more slowly, while at lower acceleration voltages (5-30 kV that are obtained in SEM), it is observed that the energy of the electron beam is not enough to provoke the reduction of Bi, being this process dependent on the energy of the electron beam.

Semi-quantitative analysis of the EDS data shows that, at first, we have very similar amounts of Na and Bi, due to the stoichiometry of the compound. Because δ-$Bi_2O_3$ is an impurity present in the $NaBiO_3$, a slightly higher amount of Bi was observed at the start of experiments (Figure 2C). After the formation of the agglomerates on the surface of the material and its subsequent degradation, an increase in the amount of Bi (91%) was observed due to the reduction of Bi (V) to metallic Bi (Figure 2F). The Cu and C elements observed in the EDS data are from the sample port. A similar behavior was found by Zheng et al.[59] in their study of the *in situ* coalescence process of Bi NPs by liquid cell TEM.

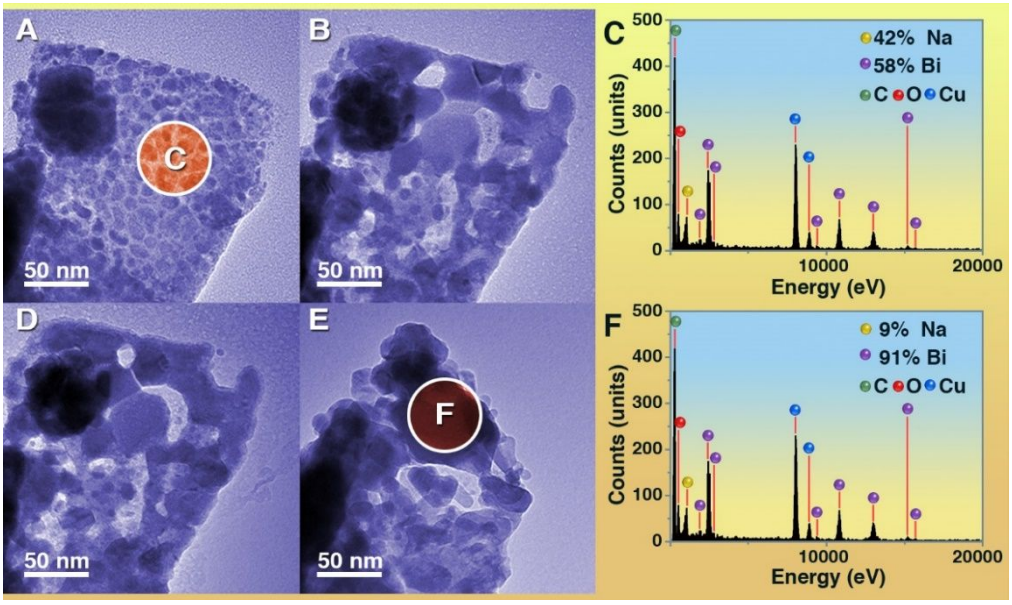


**Figure 2:** TEM image of the sample after (A) 10, (B) 15, (D) 20 and (E) 30 minutes of exposure. (C) and (F) EDS of the white circle in the image and their quantification.

High-resolution micrographs (HR-TEM) were taken to analyze the formed nanocrystals (Figure 3). Before irradiation with the electron beam, the (110) plane with an interplanar distance of 2.80 Å (Figure 3B) characteristic of hexagonal $NaBiO_3$[56] was found, and EDS analysis was performed to confirm the presence Na in the material (see supporting information, Figure S3). After 10 minutes of exposure (Figures 3C-D), small crystalline non-regular clusters appeared, and they were analyzed. The (012) plane with an interplanar distance of 3.28 Å was observed, corresponding to the rhombohedral structure of metallic Bi (Figures E-G) associated with PDF 44-1246[60] in the JCPDS database.

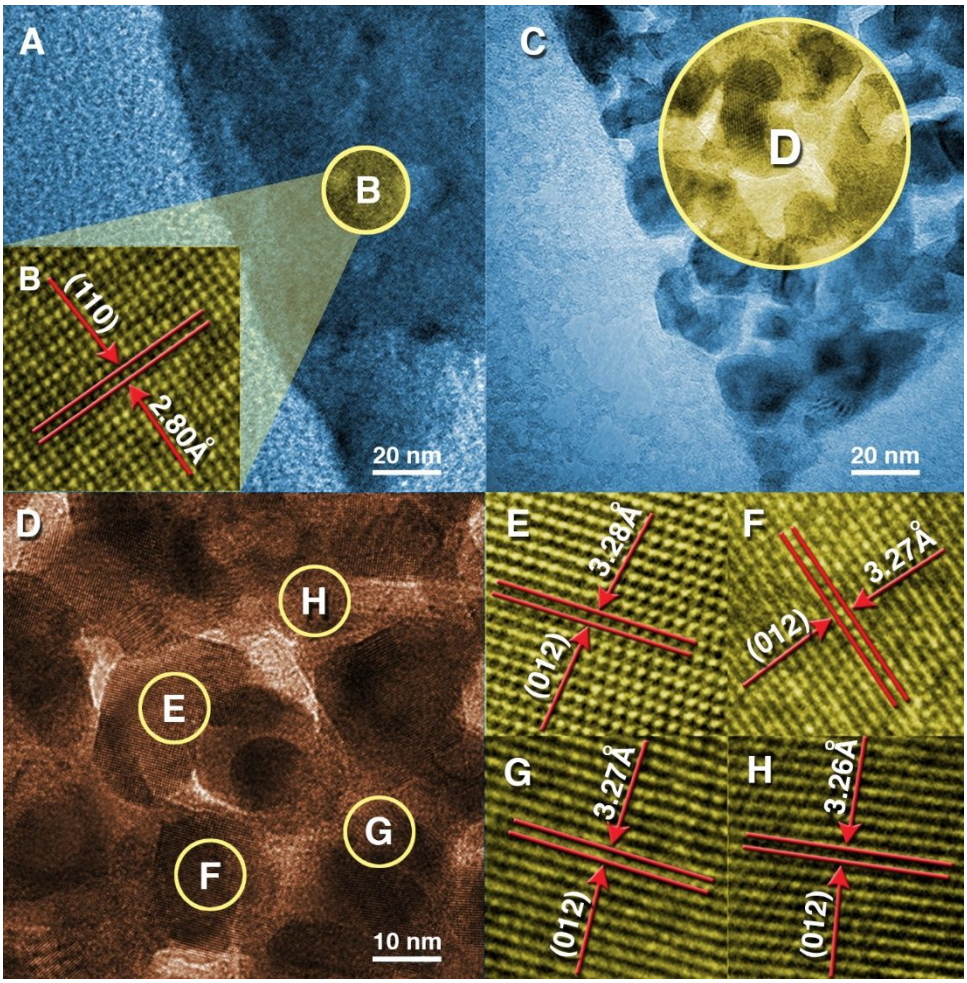


**Figure 3** - TEM image of the $NaBiO_3$ before (A-B) the irradiation by electron beam and after (C). (D) HR-TEM micrographs at higher magnification (C). (E), (F), (G) and (H) NPs of Bi rhombohedral.

Under electron beam irradiation, there is a redistribution of electrons, associated with transitions of electrons from occupied to unoccupied states in the band structure of the crystal. The occupied states in the valence band, VB, are below the Fermi level (quantum stable) and the unoccupied states in the conduction band, CB, are mostly above the Fermi level (unstable states, i.e. quantum excited states). These rearrangements induce oxidation-reduction

reactions, and in the present case, the octahedral [$BiO_6$] cluster of $NaBiO_3$ accumulates an excess of electron density, producing a continuous reduction in the oxidation state of Bi from (V) to zero (metallic Bi), via Bi (III) in $Bi_2O_3$.

$NaBiO_3$ is an n-type semiconductor. After the electron beam irradiation, the Bi-rich region becomes an n/p-type semiconductor due to the formation of internal defects caused by Bi vacancies in localized areas, thus enhancing the transfer and separation of photo-generated electron-hole pairs. Then, the action of the electron beam of the TEM induces the reduction of Bi cations in $NaBiO_3$ and the subsequent segregation of metallic Bi through the $NaBiO_3$ crystalline lattice. This creates regions with Bi vacancies ($V_{Bi}$) which function as an n-type semiconductor, and regions with oxygen vacancies ($V_O$), which function as a p-type semiconductor. The formation of this p-n junction between the xBi/$NaBi_{1-x}O_3$ heterostructure is expected to enhance the reduction activity by enhancing the conductivity, electron mobility, and lifetime of photo-generated electron-hole pairs.

A comparison with the results obtained in our previous paper which Bi NPs are obtained by femtosecond laser,[38] renders that the large number of photons generated in a femtosecond laser interacts with $NaBiO_3$ substrate, is capable to produce a plasma with high pressure and temperature values ($10^{10}$–$10^9$ Pa and 1000 K, respectively). These critical conditions allow the three distinct phases of Bi to coexist: rombohedral, cubic and tetrahedral. Hence, the present results demonstrate that the experimental conditions from the synthesis using an electron beam of TEM *in vacuum* can selectively produce the most stable rhombohedral structure of metallic Bi. This experimental observation is also consistent with the literature reporting the formation metallic Bi in a TEM. [39]

To gain a deeper insight into these experimental observations and to provide some basis upon which to understand the effects described above, a detailed theoretical study of

the electronic charge of each atom was conducted using Bader charge analysis within the QTAIM framework. Finding zero flux surfaces between two atoms allows the atomic charge to be calculated by integrating the charge density within the atomic basins, Ω, and subtracting the nuclear charge, Z, of the corresponding atom. The charge densities of the Na, Bi, and O centers as a function of the number of electrons added are depicted in Figure 4A and the values are collected in Table S1 of the supporting information. In addition, the primitive cell of $NaBiO_3$ without and with the addition of 3 and 8 electrons and the distances from their metallic centers to the corresponding oxygen atoms, i.e., the Na-O and Bi-O bond lengths, are presented in Figure 4B. An analysis of Figure 4A shows that the charge density of the Na centers is maintained, whereas the Bi centers of the $[BiO_6]$ clusters show decreasing charge densities with different behavior as electrons are added. From the addition of 3 electrons onward, the decrease in the Bi charge density becomes more noticeable.

At the same time, the two Bi−O distances start to change after the addition of 3 electrons, as can be seen in Figure SI-4 of the supporting information. The pronounced decrease in Bi charge density continues upon increasing N from 4 to 8, in which range only three Bi-O distances were found. It is interesting to note that for the $[NaO_6]$ octahedral clusters, the two Na−O distances remain almost unaltered. These findings suggest a possible decomposition of $NaBiO_3$ into $Bi_2O_3$, and then the continued reduction of Bi (III) to metallic Bi.

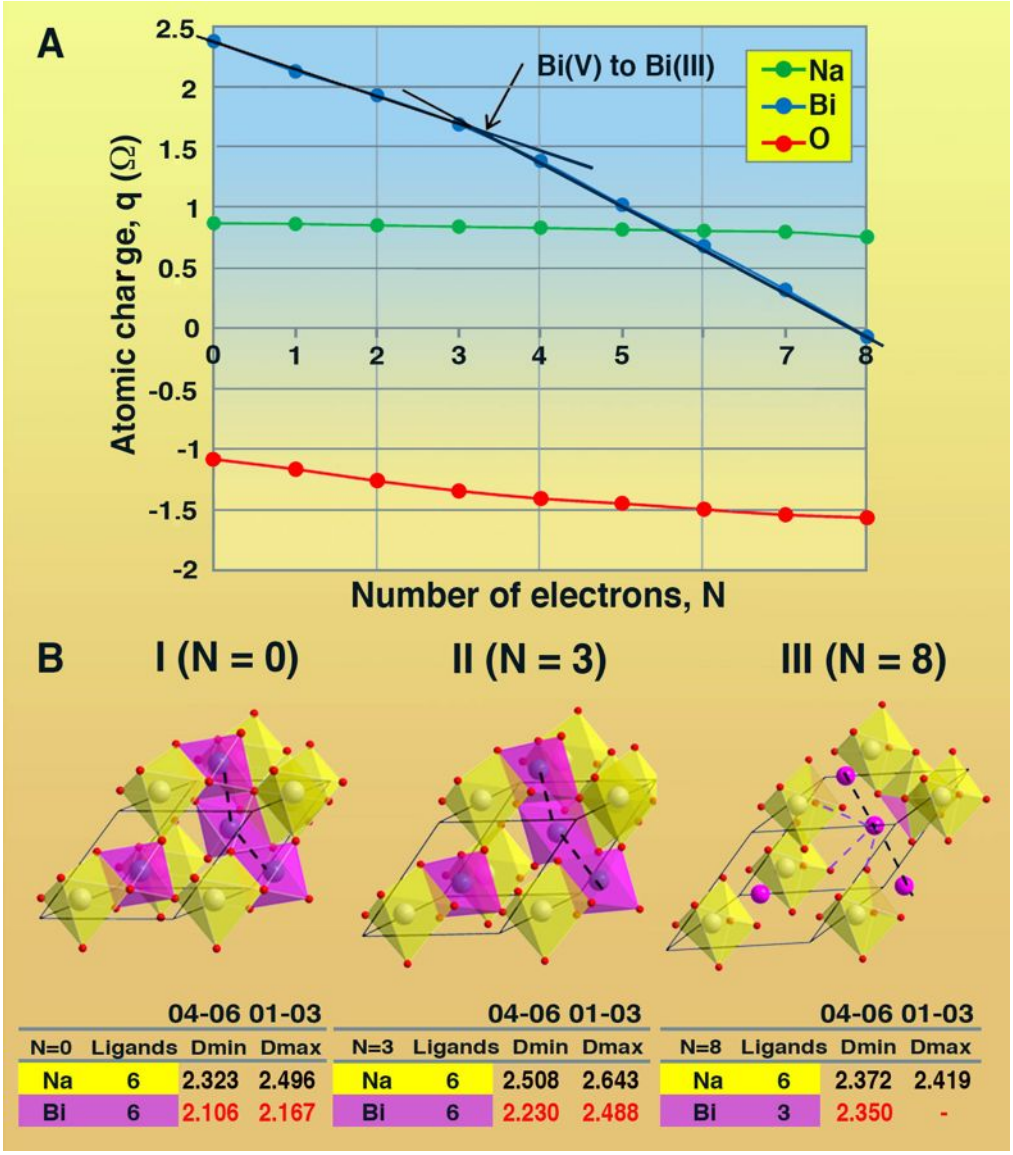


**Figure 4** - (A) Bader charge density of Bi, Na and O centers as a function of the number of electrons added. q(Ω) represents the number of valence electrons minus the calculated charge density; (B) Primitive cell without (I) and with the addition of 3 (II) and 8 electrons (III) in $NaBiO_3$ and the minimum and maximum distances in Å ($d_{min}$ and $d_{max}$, respectively) of the metallic centers to their oxygen atoms.

In Figure 5 the variation of the positions of both VB and CB is analyzed along the process of addition of electrons. First, in the neutral $NaBiO_3$ system (N=0), with the addition of three

(N=3) and eight (N=8) electrons in order to visualize the reduction in the oxidation state of Bi from (V) to Bi (III) in $Bi_2O_3$ and to metallic Bi (zero), respectively. This scheme showed in Figure 5 follows the common case of a heterojunction based on the n-type semiconductor and metal, in which at the interface of the materials electrons flow from the semiconductor into the metal to adjust the Fermi energy levels.

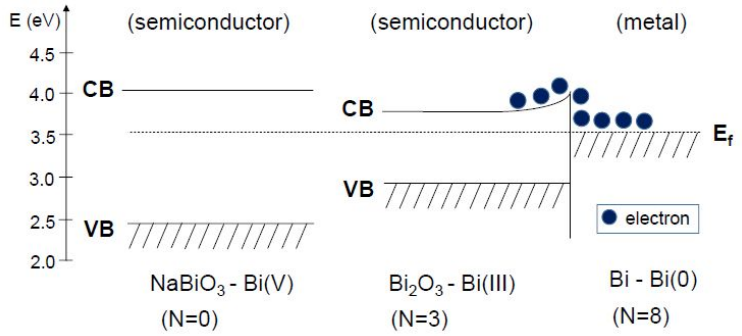


**Figure 5** - Variation of the positions of VB and CB as a function of the number of electrons added, N. The position of the Fermi energy level, $E_f$, is placed once the metallic Bi is formed.

Bader charge analysis for the tetragonal β-$Bi_2O_3$ and cubic δ-$Bi_2O_3$ structures was performed and the results are presented in Figures 6 and 7, respectively. The charge densities of the Bi and O centers as a function of the number of electrons added to β-$Bi_2O_3$ are depicted in Figure 6A, while its unit cell without and with the addition of 6 and 15 electrons and the distance between its metallic centers to the corresponding oxygen anions are presented in Figure 6B. An analysis of the results suggests that the Bi centers of the [$BiO_5$] clusters decrease their charge density gradually up to 6 electrons added, at which point the Bi coordination number changes and is reduced to three. After the addition of 6 electrons, the coordination was maintained while the Bi-O distance increased up to 2.531 Å for N=15, where the Bi atom was completely reduced (Figure S5). The charge density of the Bi and O

centers as a function of the number of electrons added to δ-$Bi_2O_3$ is presented in Figure 7A, while its cubic unit cell without and with the addition of 8 electrons is shown in Figure 7B. Bi centers of the cabin-type [$BiO_6$] clusters showed gradually decreasing charge densities up to the addition of 8 electrons, at which point the Bi atom was completely reduced, keeping the Bi coordination. At this point, the Bi-O distance increased from 2.394 Å to 2.842 Å due to the cell expansion (Figure S5). The charge density values of Na, Bi and O centers for β-$Bi_2O_3$ and δ-$Bi_2O_3$ structures are collected in Table S2 of the supporting information.

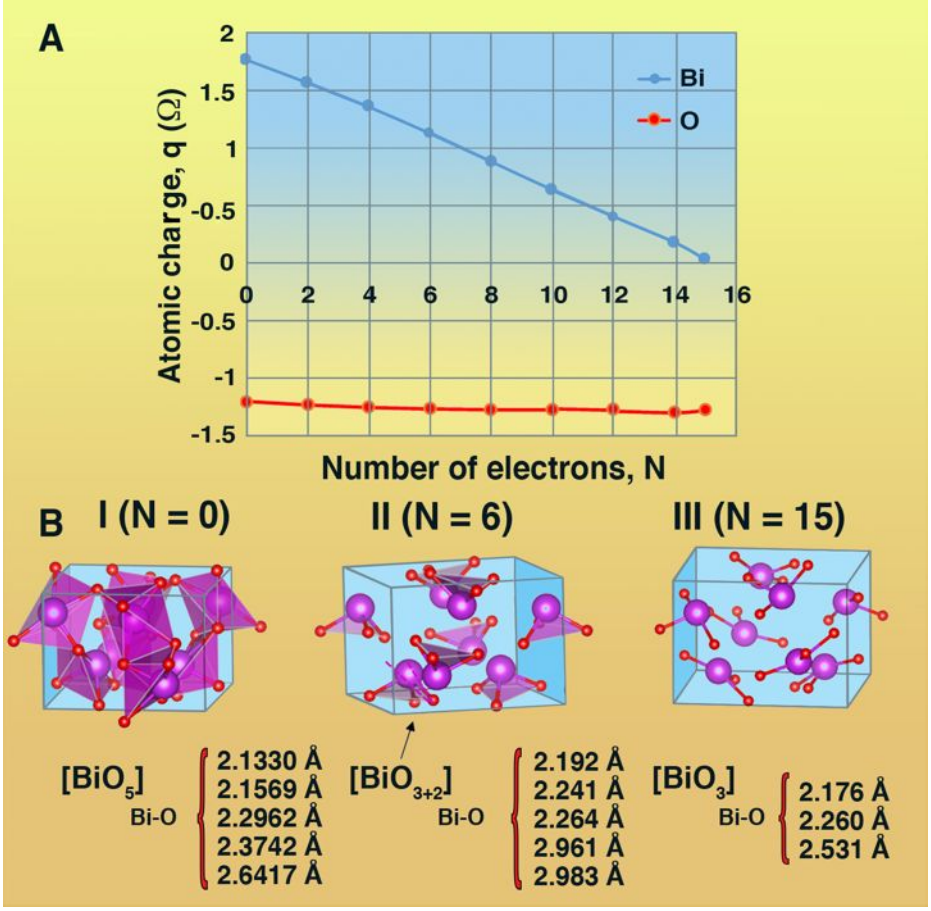


**Figure 6** - (A) Bader charge density of Bi and O centers as a function of the number of electrons added. (B) Unit cell β-$Bi_2O_3$ without (I), with the addition of 6 electrons (II) and with the addition of 15 electrons (III); and the Bi-O distances of the structural clusters.

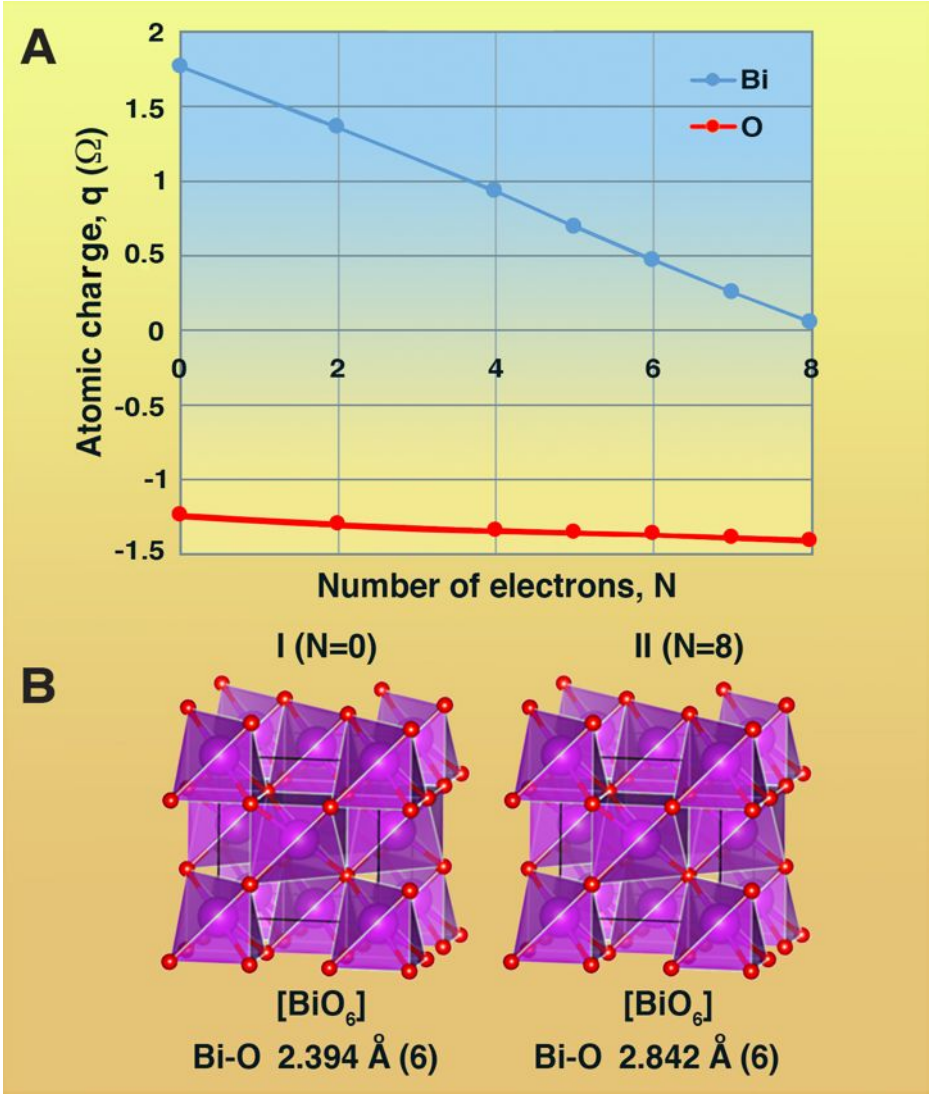


**Figure 7 -** (A) Bader charge density of Bi and O centers as a function of the number of electrons added. (B) Unit cell δ-$Bi_2O_3$ without (I) and with the addition of 8 electrons (II); and the Bi-O distances of the structural clusters.

As the transition from Bi (III) to metallic Bi was not observed during the reduction of $NaBiO_3$, the same study was performed using β-$Bi_2O_3$ as the starting reagent (Figure 8). The sample was taken to the TEM and exposed to the electron beam. After 15 minutes of exposure, crystalline clusters started to appear on the surface of the β-$Bi_2O_3$, as seen in

$NaBiO_3$. These NPs were characterized as rhombohedral metallic Bi based on observation of the (012) plane with an interplanar distance of 3.28 Å (Figure 8B), similar to the results obtained for $NaBiO_3$. The EDS analysis showed that the NPs that appeared on the surface were formed of Bi (99 %), proving that β-$Bi_2O_3$ undergoes the process of reduction from Bi (III) to metallic Bi (Figure 8C).

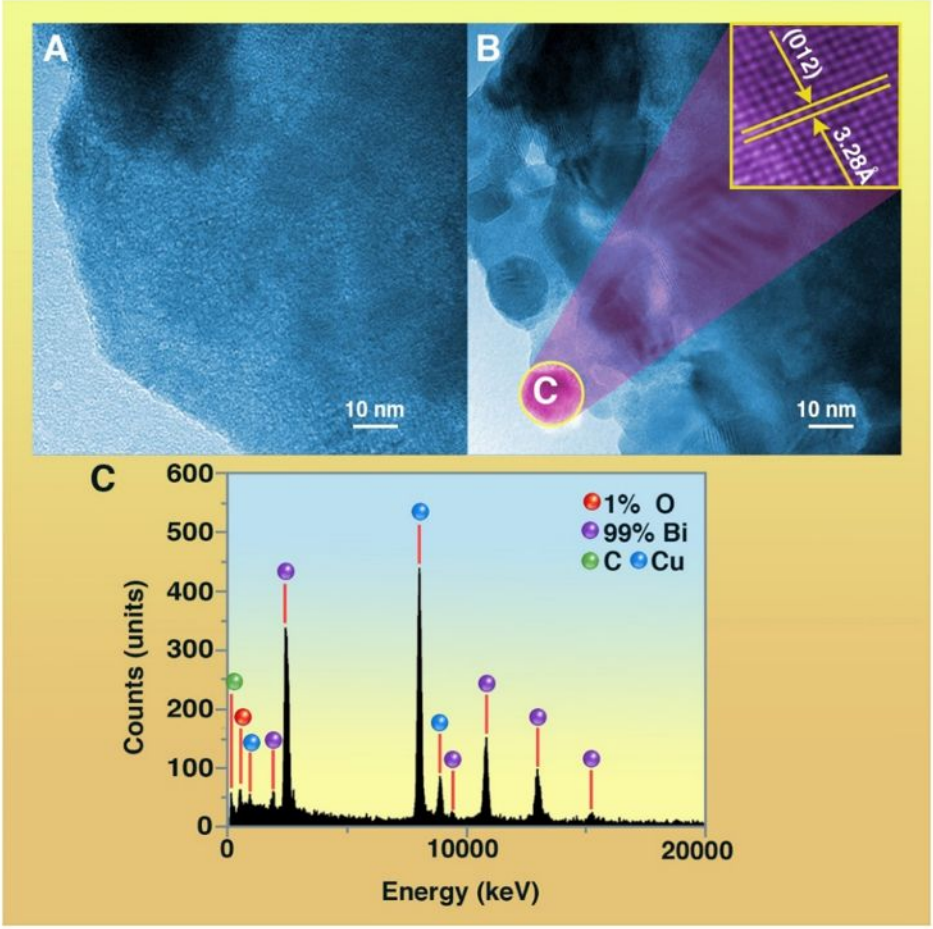


**Figure 8** - (A) TEM image of the β-$Bi_2O_3$ before the irradiation by electron beam and (B) after 15 minutes exposure. (C) EDS of the yellow circle in the image and their quantification.

## 4. Conclusions

During the process of TEM observation (interaction of an electron beam with matter), some novel phenomena were discovered. These interactions can be used to fabricate NPs and investigate their structure and chemical transformation, which is of importance for the development of novel nanostructures, especially for those that cannot be obtained using conventional chemical and physical methods.

In this work, we studied the in situ crystal growth of pure single crystals of metallic Bi on the surface of $NaBiO_3$, δ-$Bi_2O_3$, and β-$Bi_2O_3$ under the electron beam of an FE-TEM. First principles calculations at the DFT level and QTAIM analysis were combined with different characterization techniques, including HR-TEM and EDS to extend our fundamental understanding of the atomic processes that underpin the formation of Bi NPs on these materials mediated by electron beam irradiation.

The main conclusions of the present work can be summarized as follows: i) Both theoretical and experimental findings can be used to find a relationship between atomic-scale structural and electronic perturbations induced by electron beam irradiation, providing adequate conditions for the formation of Bi NPs on $NaBiO_3$; ii) Electron beam irradiation can induce the breaking of Bi-O, and to a lesser extent Na-O, bonds in the [$BiO_6$] and [$NaO_6$] clusters, respectively, as constituent building blocks of $NaBiO_3$; iii) Under electron beam irradiation, a redistribution of electrons takes place with a concomitant reduction in the oxidation state of Bi from (V) to zero (metallic Bi); iv) First, the formation of β-$Bi_2O_3$, with a Bi (III) oxidation state, takes place followed by the subsequent appearance of metallic Bi NPs; v) These structural and electronic perturbations of the material provoke a change from n-type to p-type semiconductor behavior associated to the formation of a p-n xBi/$NaBi_{1-x}O_3$ heterostructure.

With the use of robust experimental and theoretical tools, scientists now have the capability to push the limits of investigation to the ultimate level of individual atoms and single bonds. If this knowledge can be transformed to develop useful NPs, then exciting opportunities to engineer novel assemblies for new applications are wide open. The current work sheds light on the potential use of electron beams to trigger the formation of Bi and other metal NPs.

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**Supporting Information**

- XRD patters for commercial $NaBiO_3$
- Conventional and primitive cell of $NaBiO_3$ in the rhombohedral space group R-3
- EDS analysis of $NaBiO_3$
- Variation of Bi-O distances and of cell parameters in $NaBiO_3$ structure as a function of the number of electrons added, N

- Variation of cell parameters in $Bi_2O_3$ structure as a function of the number of electrons added, N. (A) β-$Bi_2O_3$ and (B) δ-$Bi_2O_3$

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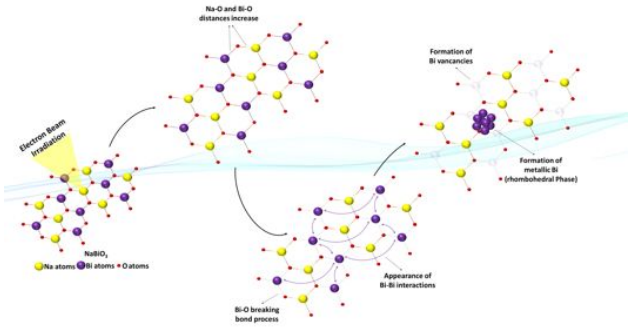
**TOC Graphic**


Na-O and Bi-O distances increase
Electron Beam Irradiation
Formation of Bi vancancies
Formation of metallic Bi (rhombohedral Phase)
Appearance of Bi-Bi interactions
Bi-O breaking bond process
Na atoms
Bi atoms
O atoms

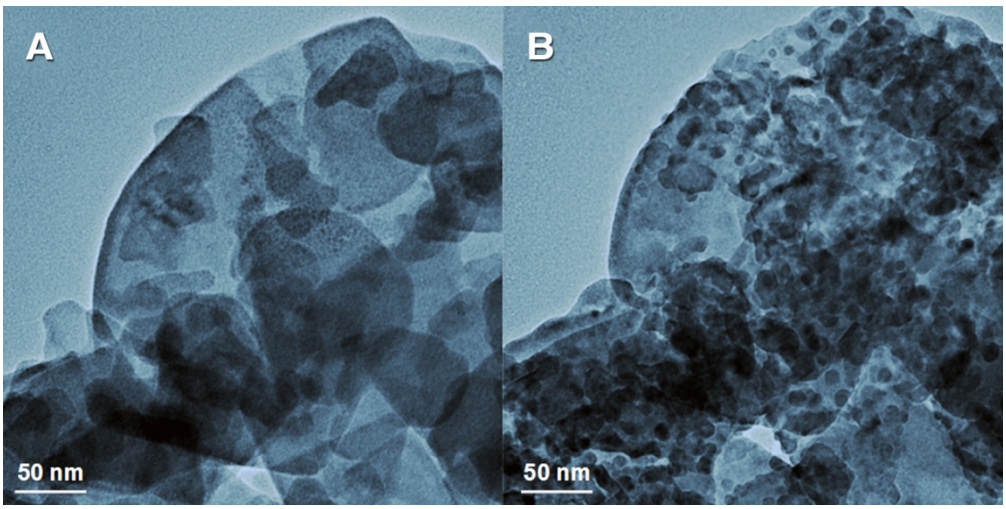



Figure 1: (A) Low-magnification TEM image of the sample before the irradiation by electron beam and (B) after 10 minutes of exposure to irradiation by electron beam.

136x68mm (300 x 300 DPI)

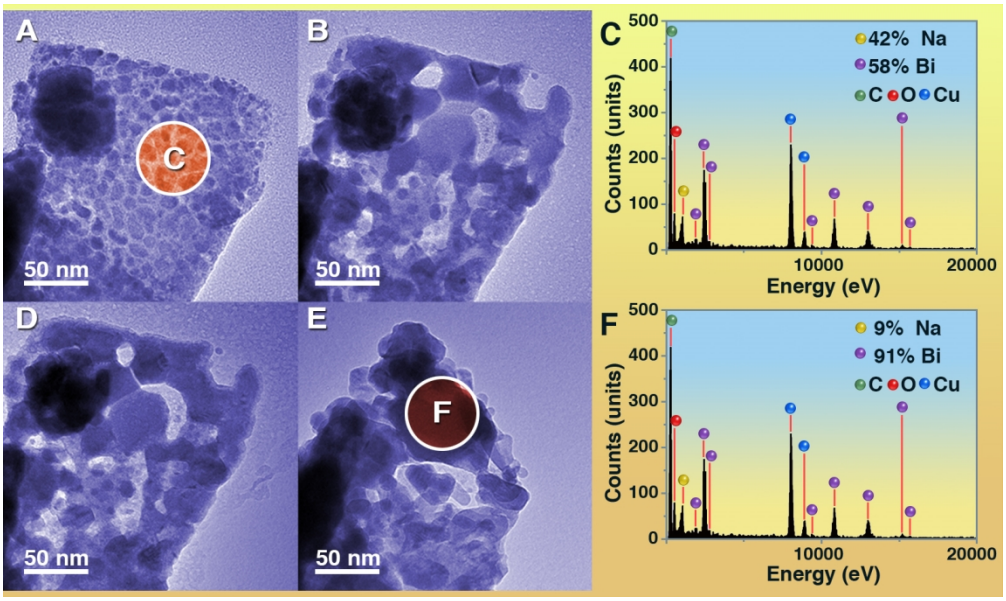



Figure 2: TEM image of the sample after (A) 10, (B) 15, (D) 20 and (E) 30 minutes of exposure. (C) and (F) EDS of the white circle in the image and their quantification.

136x81mm (300 x 300 DPI)

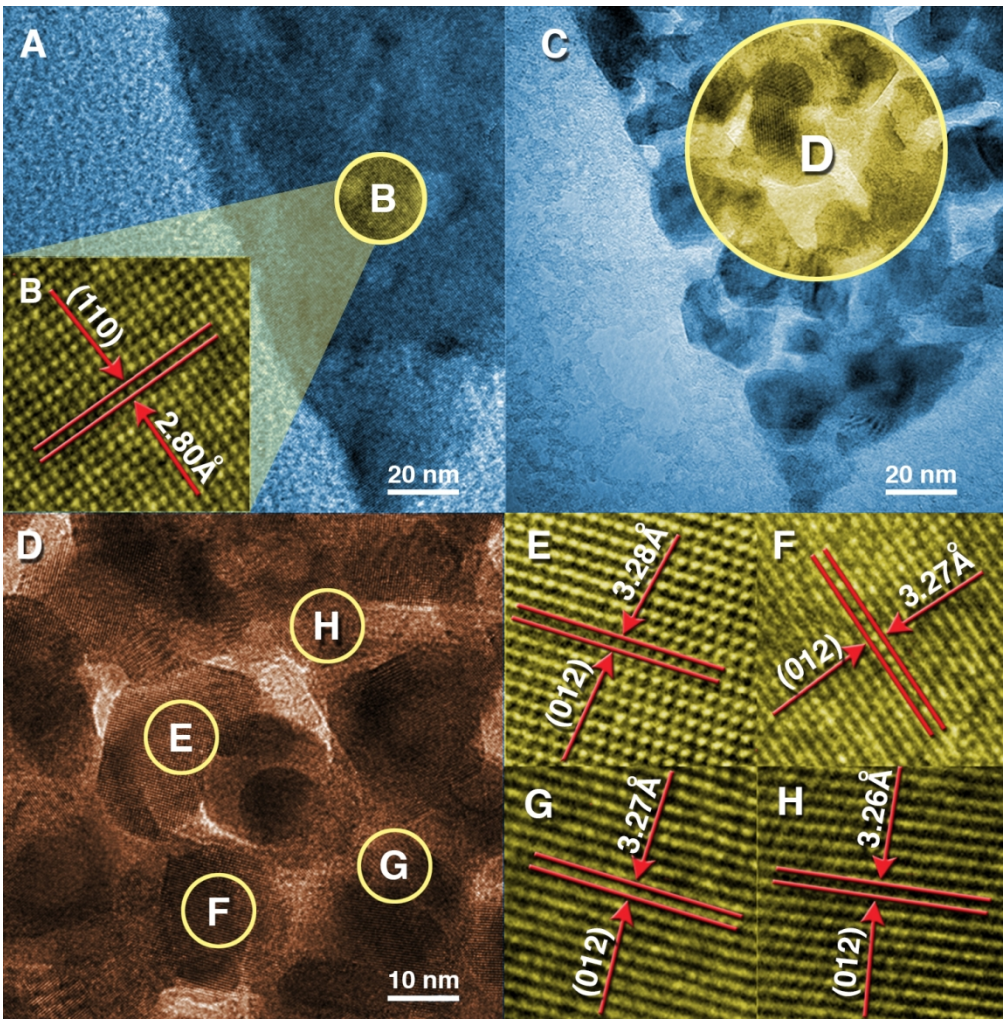



Figure 3 - TEM image of the NaBiO3 before (A-B) the irradiation by electron beam and after (C). (D) HR-TEM micrographs at higher magnification (C). (E), (F), (G) and (H) NPs of Bi rhombohedral.

127x128mm (300 x 300 DPI)

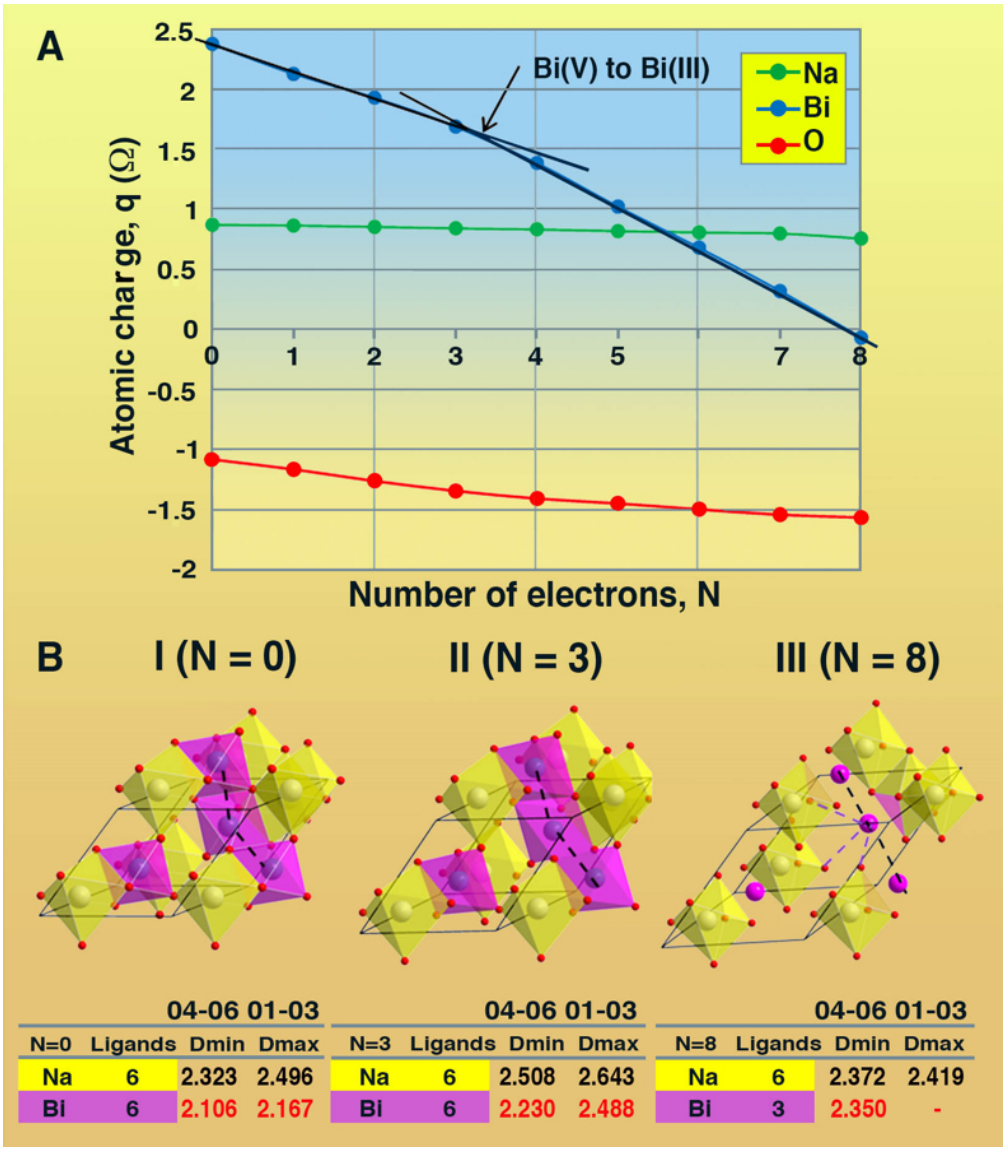



Figure 4 - (A) Bader charge density of Bi, Na and O centers as a function of the number of electrons added. q(Ω) represents the number of valence electrons minus the calculated charge density; (B) Primitive cell without (I) and with the addition of 3 (II) and 8 electrons (III) in NaBiO3 and the minimum and maximum distances in Å (dmin and dmax, respectively) of the metallic centers to their oxygen atoms.

133x151mm (150 x 150 DPI)

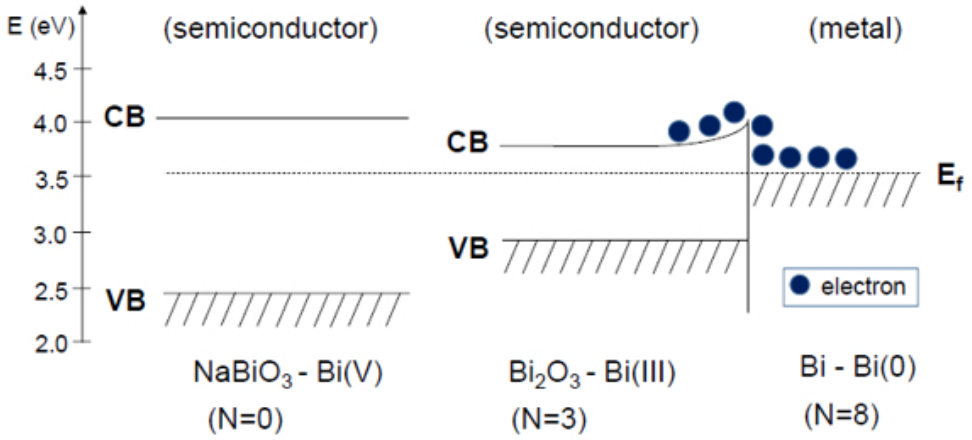



Figure 5 - Variation of the positions of VB and CB as a function of the number of electrons added, N. The position of the Fermi energy level, Ef , is placed once the metallic Bi is formed.

99x45mm (150 x 150 DPI)

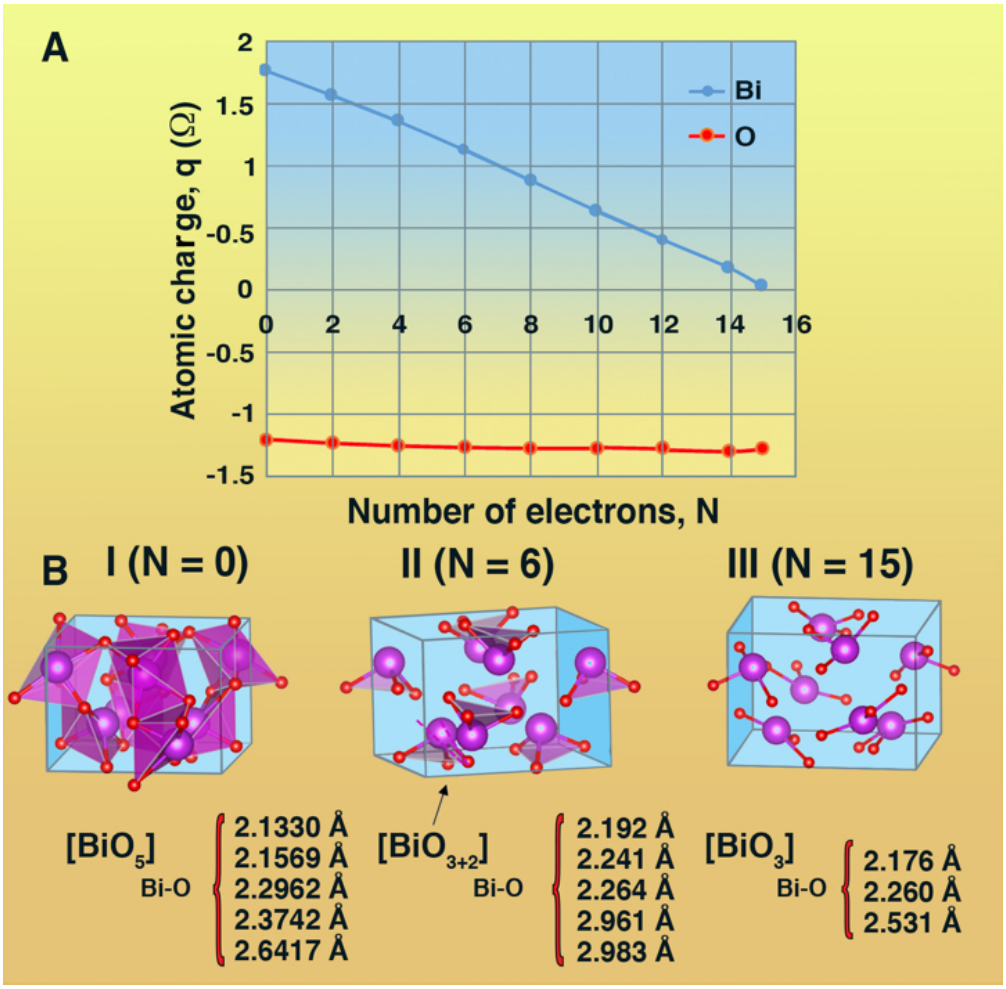



Figure 6 - (A) Bader charge density of Bi and O centers as a function of the number of electrons added. (B) Unit cell β-Bi2O3 without (I), with the addition of 6 electrons (II) and with the addition of 15 electrons (III); and the Bi-O distances of the structural clusters.

122x120mm (150 x 150 DPI)

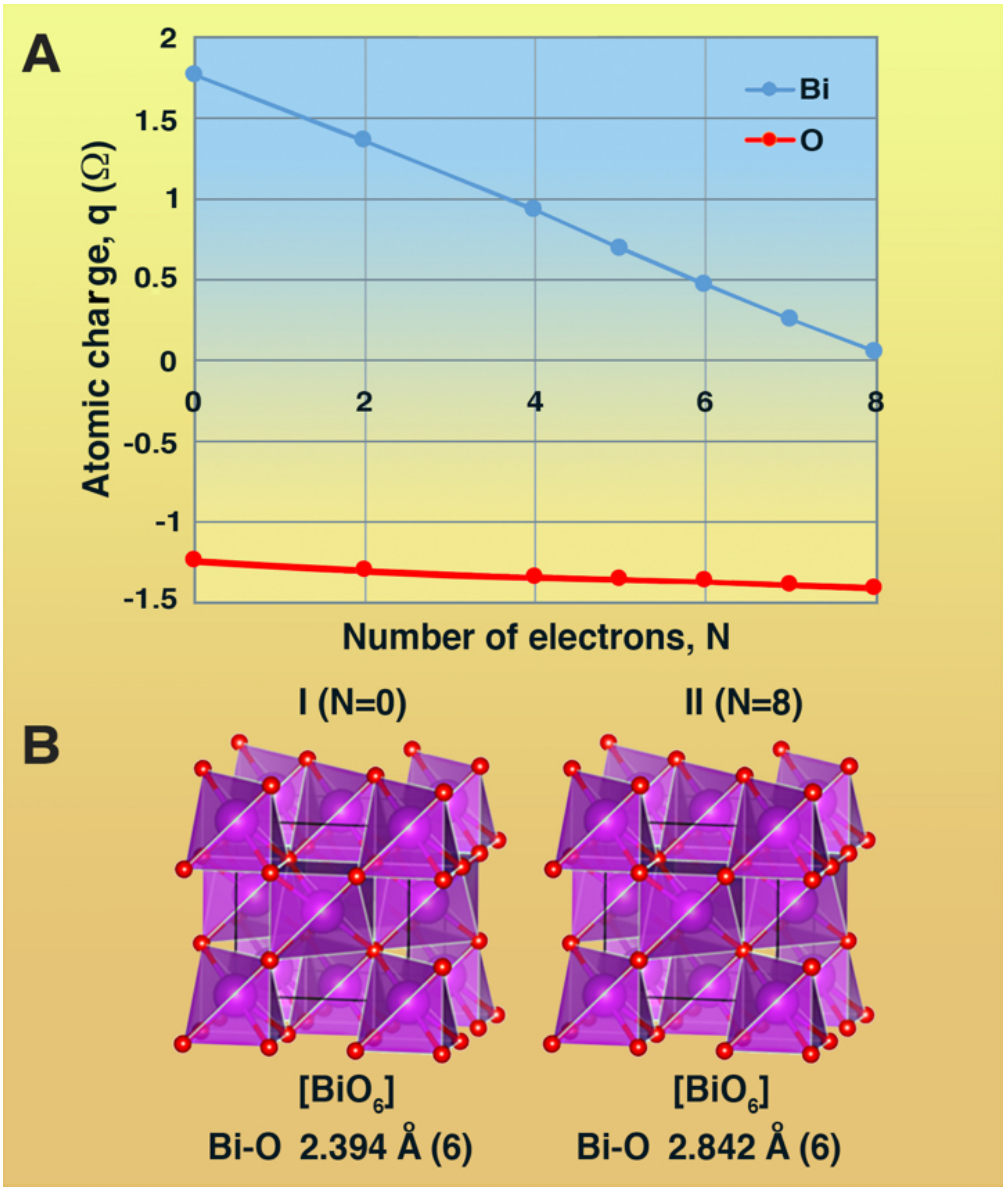



Figure 7 - (A) Bader charge density of Bi and O centers as a function of the number of electrons added. (B) Unit cell δ-Bi2O3 without (I) and with the addition of 8 electrons (II); and the Bi-O distances of the structural clusters.

122x144mm (150 x 150 DPI)

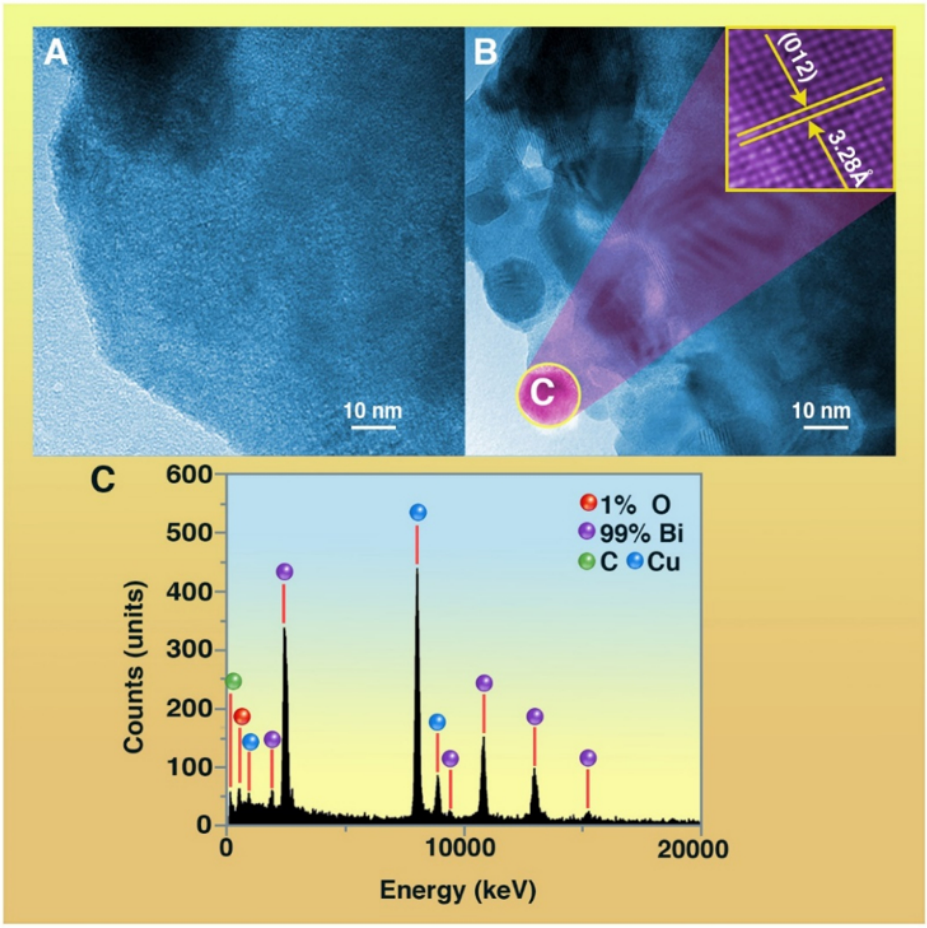



Figure 8 - (A) TEM image of the β-Bi2O3 before the irradiation by electron beam and (B) after 15 minutes exposure. (C) EDS of the yellow circle in the image and their quantification.

133x132mm (150 x 150 DPI)

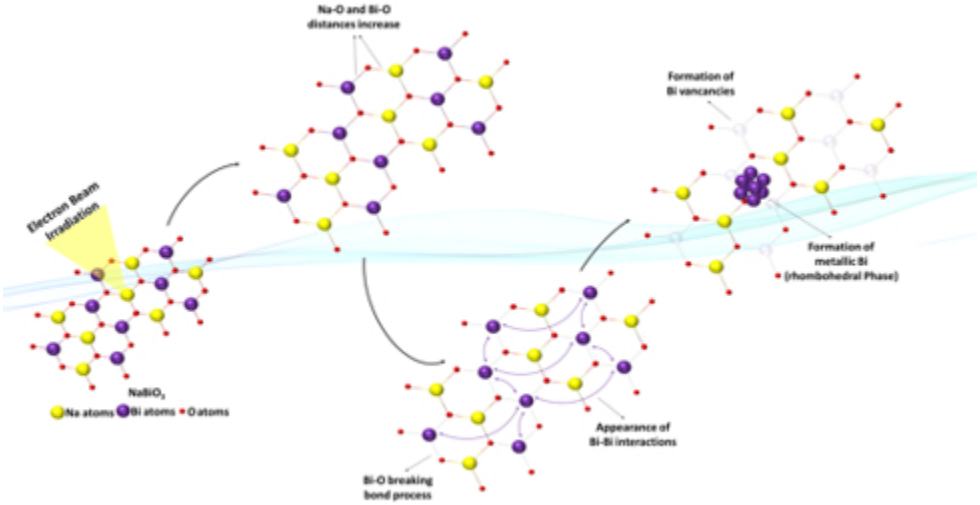



Table of Contentes (TOC) Image

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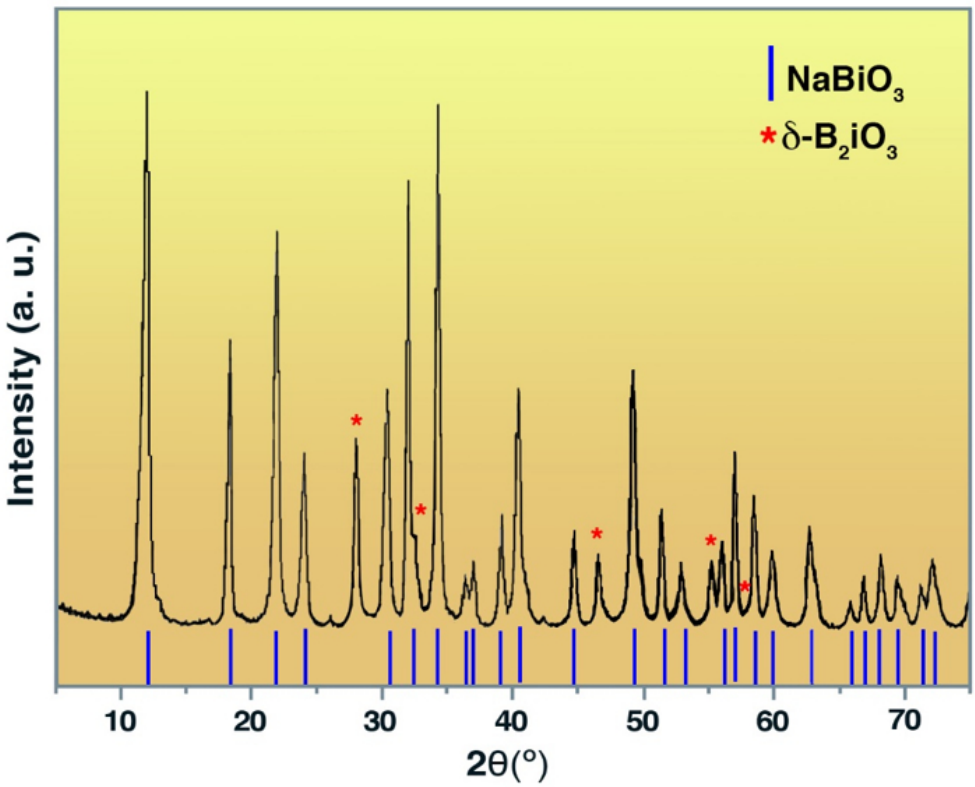
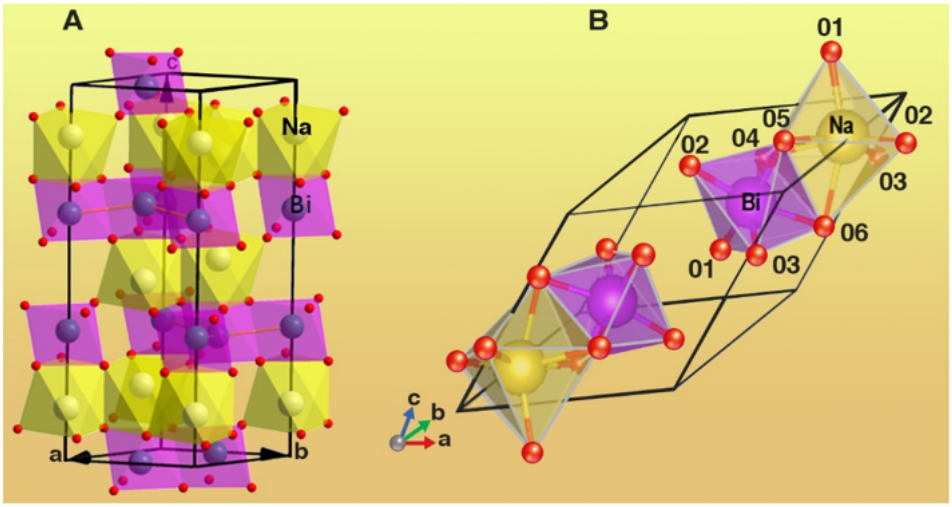



XRD patterns for commercial NaBiO3.

121x96mm (150 x 150 DPI)




Conventional (A) and primitive cell (B) of NaBiO3 in the rhombohedral space group R-3

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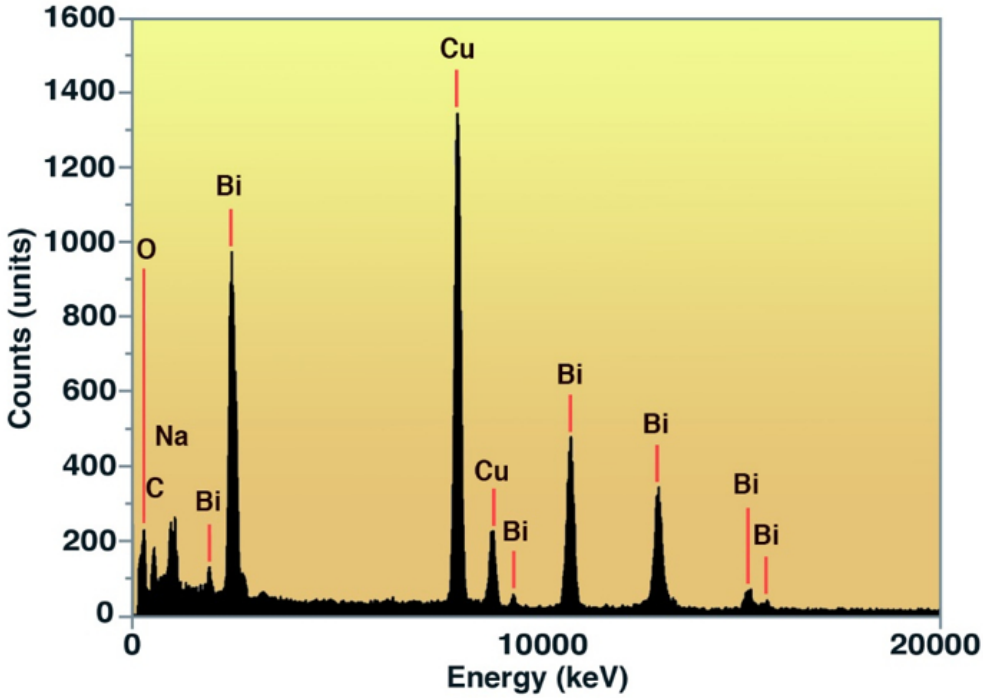
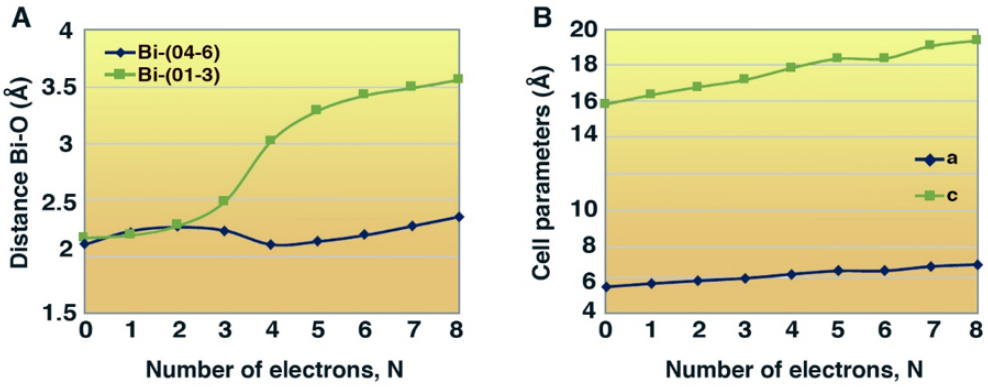


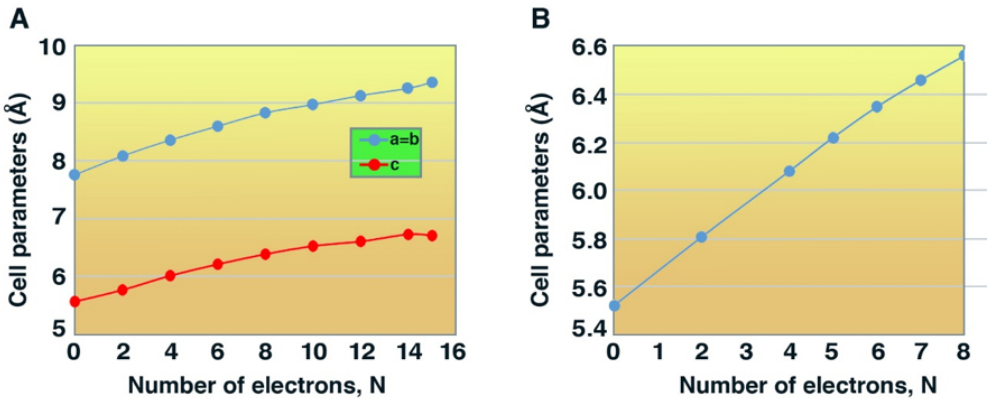

EDS analysis of NaBiO3.

118x84mm (150 x 150 DPI)




(A) Variation of Bi-O distances (B) and of cell parameters in NaBiO3 structure as a function of the number of electrons added, N.

154x63mm (150 x 150 DPI)




Variation of cell parameters in Bi2O3 structure as a function of the number of electrons added, N. (A) β-Bi2O3 and (B) δ-Bi2O3.

151x70mm (150 x 150 DPI)