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# Observation of Cotton-like Bismuth Oxide ($\beta$-$Bi_2O_{2.5}$) Prepared via Pulsed Laser Ablation Deposition

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## ABSTRACT

Monoclinic bismuth oxide ($\alpha$-$Bi_2O_3$) nanoparticles were prepared via precipitation method and irradiated with a pulsed laser forming thin films. Their phase and surface morphological properties were investigated using x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM). The XRD analysis shows the phase transformation to a partially crystalline tetragonal phase $\beta$-$Bi_2O_3$ thin film. The SEM micrograph of the nanoparticles, with an average crystal size of 72 nm, was seen to form a thin film with a peculiar structure, coined as "cotton-like", is attributed to the high surface energy absorbed by the nanoparticles during ablation. The HR-TEM micrograph shows the particulate with a clearly defined interlayer spacing.

**Keywords: Nanostructures, thin film, laser ablation, X-ray diffraction**

## INTRODUCTION

Bismuth oxide is one of the most important transition metal oxides. It plays a significant role in a modern solid-state technology due to its properties such as band gap, refractive index, dielectric properties, etc. These properties made it suitable for a large range of applications such as optical coatings, photovoltaic cells, microwave integrated circuits (George *et al*., 1987; Chopra and Das, 1983), etc. Along with these applications, recently introduced applications of $Bi_2O_3$ are in fuel cells, oxygen sensors and oxygen pumps (Switzer *et al*., 1999; Shuk *et al*., 1996 and Azad *et al*., 1994). The oxide finds extensive application as catalysts for industrial selective oxidation reactions, especially for propylene selective oxidation and ammoxidation to acrolein and acrylonitrile, respectively (Irmawati *et al*., 2004; Hanna, 2004 and Arora *et al*., 1996). This is owing to its high oxygen-ion conductivity characteristic which provides oxygen for the α-hydrogen abstraction to form a symmetric allyl intermediate (Gleiter, 1991). Hanna (2004) revealed other important role of bismuth in promoting oxygen mobility in the lattice.

In this work, $Bi_2O_3$ was prepared via precipitation method and subsequently vaporized to form a thin film. Rather than simply evaporating the material to produce supersaturated vapor, a pulsed laser ablation was used to vaporize the target material (the as-prepared $Bi_2O_3$) so as to produce a thin film which is tightly confined, both spatially and temporally. The resulting product shows a remarkable "cotton-like" structure, which to authors' knowledge, has not been reported before.

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The precipitation method is preferred in providing powders with narrow particle size distribution in the range of few nanometers (Dhage *et al*., 2003), which is crucial to most applications of nanopowders, as it provides a precisely tailored set of properties for demanding applications. More so, the properties of the respective films strongly are dependent on their structure (crystalline size and shape, phase composition, presence of amorphous phase, etc.) which in turn, are determined by the deposition method and the preparation conditions (Leontie *et al*., 2001).

## EXPERIMENTAL DETAILS

*Preparation of $Bi_2O_3$*

The Bismuth oxide nanoparticles were first prepared using the precipitation method, as reported in Patil *et al*. (2005). The Bismuth nitrate pentahydrate and standard ammonium hydroxide solution of AR grade were used for the preparation of bismuth oxide ($Bi_2O_3$). A known quantity of 4g $Bi(NO_3)_3.5H_2O$, 99.2% (HmbG chemicals) was dissolved in 50mL of 1M of nitric acid (Scharlau) and the molarity of bismuth in the resultant solution was 0.20 M. Ammonium hydroxide 25% extra pure (Scharlau) was added drop-wise to precipitate the bismuth as hydroxide. The resulting hydrate bismuth hydroxide ($Bi(OH)_3$), corresponding to JCPDS (card file number 00-001-0898), was washed several times and refluxed for 6 hours using a mantle stirrer (GLHMS 250 CC), maintaining the temperature at ≈373 K. The crystalline powder formed was dried in an oven for overnight and calcined at 673 K for 6 hours, employing the heating rate of ≈4.5 K/min. The resulting product was then characterized using the XRD, EDX and SEM.

*Preparation of the Thin Film*

To prepare the thin film, 0.5g of the as-prepared $Bi_2O_3$ was compressed into round pellet shape, using a hydraulic press with a force of 5 kN, irradiated using a pulsed laser and deposited onto unheated glass substrates. In the experiment, an Nd: YAG laser with wavelength 532 nm and a pulse-pulse width of 140 ns was used. The power, current, pressure and frequencies used were 10.24W, 25A, 5 Torr and 5 kHz, respectively (detailed steps on the setup was published elsewhere by Noorhana *et al*., 2005). The reaction process was carried out in an inert atmosphere, under the influence of Argon flown at 250 mL/min.

During the vaporization process, the flowing argon gas sweeps the produced soot from the target onto the substrate located 3cm away and parallel to the target. Furthermore, the gas leads to the confinement of the plume and a deceleration of the ablated particles, which consequently decreases its cooling rate. The process involves the bombardment of photons on the target material, leading to the emission and condensation of the particles on the substrate. The entire process includes the formation of the plasma plume with high energetic species and the subsequent transfer of the ablated material through the plasma plume onto the unheated substrate.

*Characterization Techniques*

For the x-ray diffraction (XRD) measurements, Philips X'Pert-MPD diffractometer, equipped with $CuK_\alpha$ target, operating in ambient temperature at 40kV and 30 mA, was used to generate diffraction patterns from the samples in ambient temperature, at a scanning rate of 0.33°/min for 2θ from 20° to 80°. The SEM was performed using the ZEISS SUPRA 35 VP FESEM equipped with the EDX. The SEM micrographs performed using field emission gun operating at 5-15 keV, while EDX was performed with a noise level of 40 eV. Meanwhile, the HR-TEM was performed using Philip Tecnai 20, with an accelerating voltage of 200kV. The densities and surface area were measured

using AccuPyc1330 helium Picnometer and BELSORP-mini high precision measuring apparatus, respectively. The crystallite size was calculated using the Scherrer's equation.

$$D_{hkl} = \frac{k\lambda}{B \cos \theta} \text{ Å} \quad (1)$$

where '$\lambda$' is x-ray wavelength (1.542 Å), $\Theta$ the Bragg's angle at which the peak is observed, and '$B$' is the full width of diffraction line at half of the maximum intensity.

## RESULTS AND DISCUSSION

The structural analysis of the bismuth oxide films was carried out at varying diffraction angles $2\theta$ from 20° to 60°, as shown in *Fig. 1a*. The observed values were in good agreement with the standard values in JCPDS card file number: 01-071-2274, confirming the formation of monoclinic $\alpha$-$Bi_2O_3$. The crystallite size of (-1 2 1) plane-oriented $\alpha$-$Bi_2O_3$ particles were estimated using the Debye Scherer's formula and was found to be about 124.4 nm. The calculated lattice parameters by the least square fit are $a$ = 5.8486Å, $b$ = 8.1661Å and $c$ = 7.5059Å, and the cell volume (V) calculated from monoclinic crystal V = abc sinβ was found to be 330.15$Å^3$.

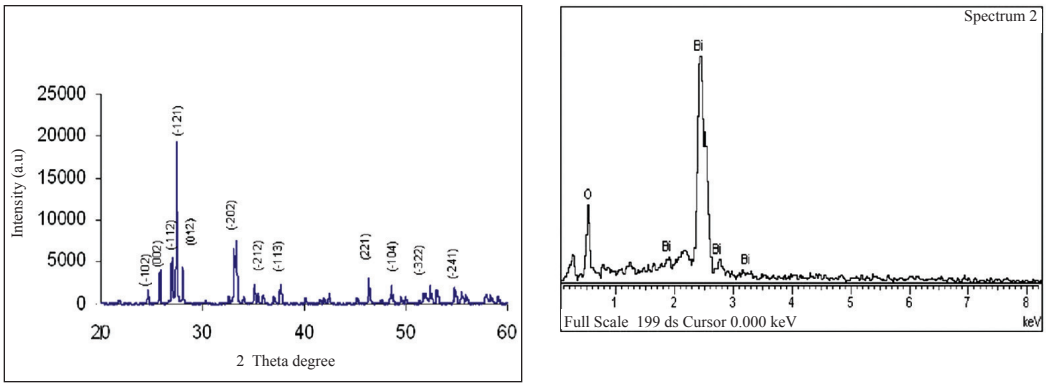


*Fig. 1: (a) XRD pattern and (b) EDX profile of the as-prepared α-$Bi_2O_3$ nanoparticles*

*Fig. 1b* reveals that the sample is of high purity, as only Bi and O peaks were visible in the spectrum. Furthermore, a close correlation was observed in the theoretical and experimental weight percent, having 11.20 and 10.30 wt% for oxygen and 88.80 and 89.70 wt% for bismuth for the observed and theoretical values, respectively.

*Fig. 2* shows the SEM micrograph of the as-prepared α-$Bi_2O_3$. It can be seen that the sample is a flake-like structure described by vectors of unequal lengths. This structure is in agreement with the XRD result, which describes the sample as monoclinic. The size of the particles, as revealed by the SEM, ranges from 50 – 100 nm. The slight discrepancy observed with the calculated value using the XRD result is attributed to the non-ideal situation in the crystals, as against the assumptions of the Scherer's formula. Such inherent factors as crystal imperfections were not taken care of by the Scherer's formula. Acknowledging the fact that density is a fundamental parameter contributing to the characterization of a product, the density of the resulting product as recorded by AccuPyc1330

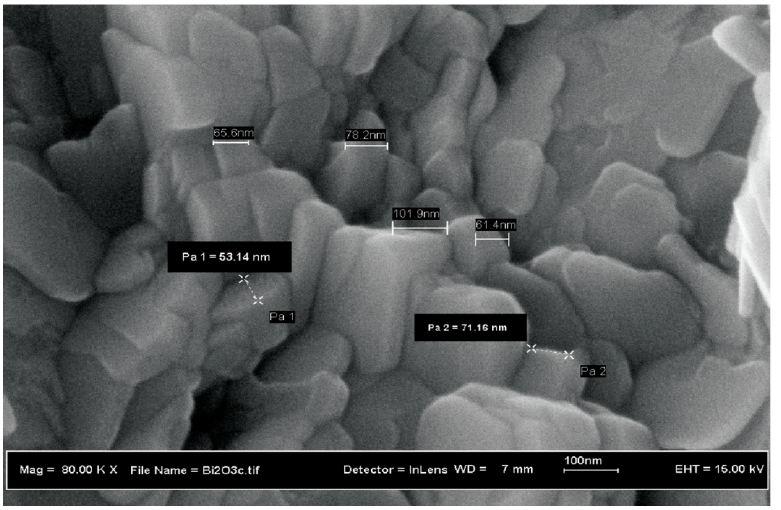


*Fig. 2: SEM micrographs of the as-prepared α-$Bi_2O_3$ nanoparticles*

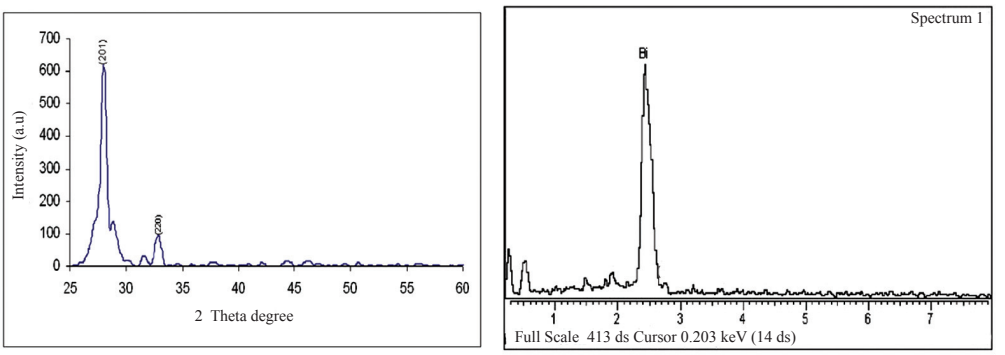


*Fig. 3: (a) XRD pattern and (b) EDX spectrum of the deposited "cotton-like" β-$Bi_2O_{2.5}$ thin film*

Picnometer was 8.91g/cm$^3$, which is very close to the theoretical density of the bismuth oxide (8. 90g/cm$^3$). The BET surface area of the oxide was 0.836m$^2$/g.

For the XRD pattern of the thin film as shown in *Fig. 3a*, it reveals a change of phase of the $Bi_2O_3$. The highly crystalline monoclinic α-$Bi_2O_3$ changes to a partially crystalline tetragonal non-stoichiometric phase β-$Bi_2O_{2.5}$ corresponding to standard values in JCPDS card files number: 01-074-1999. Consequently, the deficiency of oxygen atoms may have led to the formation of $Bi_2O_{2.5}$ phase in the film (Gujar *et al*., 2006). The amount of oxygen required for the phase formation is dependent on the thermodynamic stability of the desired oxide phase (Norton, 2004). The interaction of ablated species with the background gas produces sub-oxide species in the ablation plume. These sub-oxide species facilitate oxide phase formation. In addition to actively participating in the chemistry of the bismuth oxide growth, the background gas reduces the kinetic energies of the ablated $Bi_2O_3$. This means that with further annealing, $Bi_2O_{2.5}$ may be converted into $Bi_2O_3$ by taking oxygen from the surrounding medium.

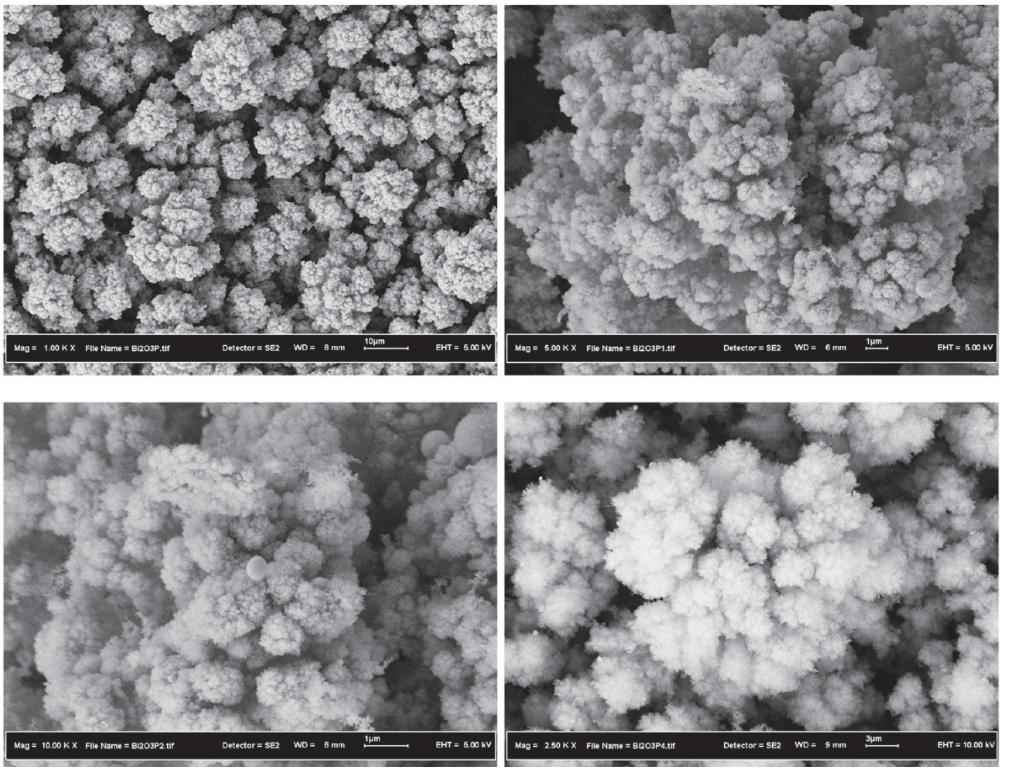


*Fig. 4: SEM micrographs of the "cotton-like" β-$Bi_2O_{2.5}$ thin film with different magnifications (a) 1000 X, (b) 5,000 X, (c) 10,000X and (d) 2,500X*

The XRD pattern of the as-deposited film revealed a partially crystalline structure. A reduced intensity of the thin film was observed, and this could be attributed to the formation of dangling bonds in the thin film deposited onto the glass substrate. This also suggested that the dangling bonds had given a rise to the interface states within the energy band gap of the glass consequence to the ablation process. The partially crystalline film growth depends on the surface mobility of the bismuth adatom (vapour atoms). Normally, the adatom diffuses through several atomic distances before sticking to a stable position within the newly formed film (Xu *et al*., 2006), and thus, the surface temperature of the substrate determines the surface diffusion ability of the adatom. High temperature favours rapid and defect free crystal growth, whereas low temperature or large supersaturation crystal growth may be overwhelmed by energetic particle impingement, resulting in disordered or even amorphous structures.

The EDX spectrum of the deposited thin film, shown in *Fig. 3b*, further confirms the presence of bismuth and oxygen in the sample. The surface morphology of as-deposited $Bi_2O_3$ thin films was studied from the SEM micrographs given in *Fig. 4*. At lower magnifications, the micrographs (*Fig. 4a* and *4b*) showed some spherical-like structures for the deposited film with defined nucleation points; however, a careful observation at high magnification (*Fig. 4c* and *4d*) showed the presence of well-grown "cotton-like" structures. These structures can be attributed to the properties and the composition of the plume evolved in this short time as a result of collisions between the bismuth particles within the plume and interaction between the plume and the laser. The

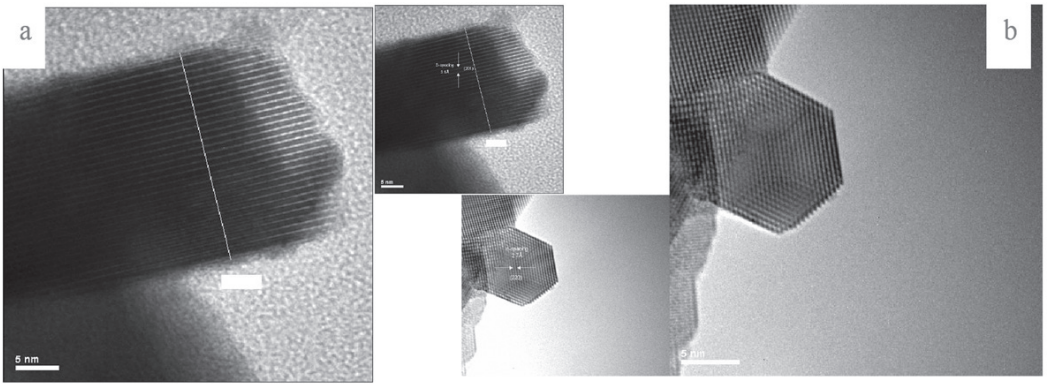


*Fig. 5: HR-TEM micrograph of the deposited "cotton-like" $Bi_2O_{2.5}$ thin film (a) d-spacing of 3.1Å (b) average d-spacing of 2.7Å*

components of these bismuth particle layers, (ions, electrons, atoms, radicals or clusters), travel at an extreme speed through the vacuum chamber until they have impinged on the surface of the substrate.

Since the sensitivity of a thin film is dependent both on the nature and the condition of the target material, and on the laser pulse parameters such as the wavelength, intensity, fluence, pulse duration, etc. (Satyanarayana *et al*., 2007)), the low melting point of the target material ($Bi_2O_3$), which is 817ºC and the high intensity of the Nd: YAG laser used for this work (5.2kW/cm$^2$) resulted in this wonderful structure. Further observation revealed a change in the density as a consequence to the ablation, and the resulting density of the thin film is 16.3844 g/cm$^3$. The increase in the density (as observed in the thin film) was attributed to the decrease in the bismuth-oxygen ratio, in addition to the decrease in the particle size of the resulting thin film. A tremendous increase in the BET surface area to 6.7304m$^2$/g was also observed, a situation attributed to the decrease in the crystal size consequent to ablation process.

To have a closer look at this cotton-like structure, the HR-TEM was used. The HR-TEM image of the deposited thin film (*Fig. 5a*) shows a clearly defined d-spacing, with an average d-spacing of 3.1Å, as estimated by the J-image software running on Linux. In *Fig. 5b*, the result exhibits a hexagonal shaped structure with an average d-spacing of 2.7Å. Abstracting the data from the XRD data in *Fig. 3(a)*, the values of *Figs. 5(a)* and *5(b)* were found to correspond to (201) and (220) planes, respectively.

When the dimensions were decreased from the micron level to the nano level, the specific surface area was found to increase by 3 orders of magnitude. In such a case, large proportions of the atoms will either be at or near the grain boundaries (Suryanaraya, 2005). Consequently, the quantum confinement would result in photocatalytic activities consequence to the immobilization of the high surface area nanostructures. These results suggest that the as-prepared bismuth oxide thin film would find the application in facilitating oxygen mobility in the oxide lattice in catalysis, and also result in a small shift of the reduction maximum toward lower temperature (Liu *et al*., 2003). Within the molecular sheets of bismuth, the intermolecular forces are involved in the covalent bonding and the forces between the sheets are primarily Van der Waals bonds (Evans, 1964). Due to the quasi-layered structure of elemental Bismuth, the formation mechanism of the Bi nano-

tubes reported by Liu *et al*. (2003), the observed structure might also be catalytically useful in the growth of carbon nanotubes. However, this view is still limited and further study is in progress.

## CONCLUSIONS

Pure phase monoclinic α-$Bi_2O_3$ of an average crystal size of 72 nm was obtained using the gel-precipitation technique and the bismuth oxide thin films were prepared using a pulsed laser ablation technique. The as-prepared films were polycrystalline with the phase of tetragonal β-$Bi_2O_{2.5}$. The surface morphological study revealed the total coverage of substrates with well-developed grains. From the SEM studies, a "cotton-like" structure was observed for the bismuth oxide films. The HR-TEM micrographs showed a clearly defined d-spacing and the ablation process was seen to result in the break up of the particulate of the as-prepared α-$Bi_2O_3$ to a tetragonal β-$Bi_2O_{2.5}$ with average grain sizes of 10 nm as deposited on the substrate. This means the effect of the ablation process, with the power of 10.24 W, resulted in further breaking up of the Nanoparticles and a change of phase. The large surface area consequence to the small size structure is believed to result in an improved reactivity and diffusivity.

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