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Synthesis and characterization of Bismuth oxide nanoparticles via sol-gel method

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Abstract: - Bismuth oxide nanopowders were prepared by the sol gel method. The overall process involves three steps: formation of homogeneous sol, formation of gel and decomposition of the gel to obtain raw powders. The nanocrystalline materials were obtained after calcination the powders at 500°C which is lower than the sintered temperature of the conventional solid-state method. As-prepared bismuth nanopowders were characterized by x-ray diffraction (XRD), FT-IR and FESEM (scanning electron microscopy analysis).Transmission electron microscope (TEM) investigations revealed that the average particle size is less than 20 nm.

Keywords*: Bismuth oxide; Sol-gel; Nanopowders; Electron microscopy*

I. INTRODUCTION

Bismuth oxide (Bi_2O_3) has been investigated extensively due to its optical and electrical properties such as refractive index, large energy band gap, dielectric permittivity as well as remarkable photoluminescence and photoconductivity. These properties make bismuth oxide an interesting candidate for applications in the fields such as optoelectronics, optical coatings, and gas sensors [1]. The synthesis of bismuth nanoparticles has been recently reported by using a chemical method [2].There exists five polymorphs of bismuth oxide (Bi_2O_3) named: α-Bi_2O_3 (monoclinic), β- Bi_2O_3 (tetragonal), γ- Bi_2O_3 (BCC), δ-Bi_2O_3 (Cubic), ε-Bi_2O_3 (triclinic). α-Bi_2O_3 transforms in to δ-Bi_2O_3 at 729°C [3-4]. The cooling of the δ-Bi_2O_3 phase gives rise to the β-Bi_2O_3 at 650 °C or the γ- Bi_2O_3 at 639 °C. The low-temperature α-phase and high-temperature δ-phase are stable, and the others are high-temperature metastable phases such as β-Bi_2O_3 and γ-Bi_2O_3, these can be stabilized to exist at room temperature by doping with impurities. N.Cornei et al. have recently reported the synthesis of a new phase named ε-Bi_2O_3 by using the so called hydrothermal method [5].The authors found that this polymorph is an ionic insulator in contrast to β-, γ-, δ-Bi_2O_3 (ionic conductors). In the present work we report new results of the synthesis of Bi_2O_3 polymorphs using a sol–gel procedure [6].This method is commonly used for preparation of oxides [7].

Using chemical methods, e.g. co-precipitation, sol–gel, hydrothermal technique have been confirmed to efficiently control the morphology and chemical composition of prepared powders and it can reduce the sintering temperature[8].This process involves of metal ions by poly functional carboxyl acids, such as citric acid that was used in this work.

II. EXPERIMENTAL

2.1. Raw materials

Bi $(NO_3)_3.5H_2O$ (98% in purity), HNO_3 (67.5% in purity), citric acid (AR grade), PEG600 H $(OCH_2CH_2)_n$ OH, were purchased from Merck and used as received.

2.2. Devices

XRD diffraction studies were carried out by Philips (PW3710) diffractometer with CuKα
Radiation source (λ=0.151478 nm).The TEM picture was recorded with Zeiss EM 10C instrument at the accelerating voltage of 100 kV. IR transmittance and absorption spectra were measured on the two samples prepared by KBr pellet technique in the wave number range of 400–4000 cm^{-1} on (FTLA 2000-100) model.
Field emission scanning electron microscopy measurements studies were performed using Hitachi S4160 model.

2.3. Synthesis

Bismuth nitrate and citric acid were used for the preparation of Bi_2O_3 are of AR grade. A known quantity of $Bi(NO_3)_3.5H_2O$ was dissolved in nitric acid solution and mixed with citric acid in a 1:1 molar ratio. In order to prevent agglomeration, a small amount of PEG600 was added as a surfactant. The pH value of the solution was adjusted to 3.
The above solution was stirred for 2 h, and then a sol formed. The sol solution was heated to 80 °C for 3h to form a yellowish gel. This gel was decomposed at 120°C in oven .The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consists of homogeneous flakes of very small particle size.

III. RESULTS AND DISCUSSION

XRD were employed to characterize these powders. The sample was scanned in the 2θ range of 4˚-60˚ for a period of 5 s in the step scan mode. The diffraction pattern (Fig.1) presents peaks corresponding to reflection planes of the monoclinic structure of metallic bismuth.A small fraction of unidentified phase(s) was observed.
The average crystallite size which has been determined by Debye-Scherrer formula:

Where L is coherence length, related to spherical particle diameter D=4/3L, λ is the wavelength of X ray (nm), k is a constant (= 0.9 assuming that the particles are spherical), β is the full width in radius at half-maximum (FWHM) of the Highest peak (rad) and θ is the Bragg angle of the highest peak. The particle size obtained from XRD data is 40 nm. The calculated lattice parameters by least square fit are a=5.8400 Å, b= 8.16600 Å, c = 7.5100 Å.

Figure 2(a-c) shows SEM images of the bismuth samples treated at 200, 500 and 800 ºC, respectively. Figure 2a exhibits a pseudospherical morphology; however these particles begin to form agglomerates when the temperature within the thermal treatment increases up to 800 ºC (Fig. 2c). After a thermal treatment at 800 ºC the size of the particles has changed to micro-spheroid as can be clearly seen in figure 2. The grain sizes estimated from SEM observations were different from those done by means of Scherrer's equation. This equation assumes that all the crystallites are of the same size, but in an actual specimen, the size range and distribution affect β.

The fine powders were dispersed in acetone and were put on a carbon coated TEM copper grid. The TEM image of the superfine Bi_2O_3 powder (Fig. 3) shows that Bi_2O_3 nanoparticles are spherical-like shape, and the average particle size are less than 50 nm, which was in good agreement with the XRD result.

The IR spectra of the dried gel and calcined powders of bismuth oxide are shown in Figure 4(a, b). After drying at 120°C, the spectrum is complex due to the existence of lots of organic compounds. Band at 3500 ~ 3200 cm^{-1} is a characteristic group frequency from the stretch vibration of O-H [9]. The broad band at 2800~ 3200 cm^{-1} comes from C-H stretch vibration and the stretch -CH_2 of located at 2930 cm^{-1}. The peak of 1386.02cm^{-1} is the characteristic ones of NO_3^- group. The broad one around 700 ~ 400 cm^{-1} originates from the metal-oxygen (Bi-O) vibration. After annealing at 500°C, many vibration lines disappear because of the evaporation of most solvents and decomposition of the organic ingredient. Samples before or after anneal have the same absorption positions but different intensity.

IV. CONCLUSIONS

In summary, homogeneous bismuth oxide nanopowders have been prepared by sol gel method. The single α-phase is obtained at a temperature lower than that prepared by conventional solid state method. The average size of these nanoparticles ranges less than 20 nm.

Figures

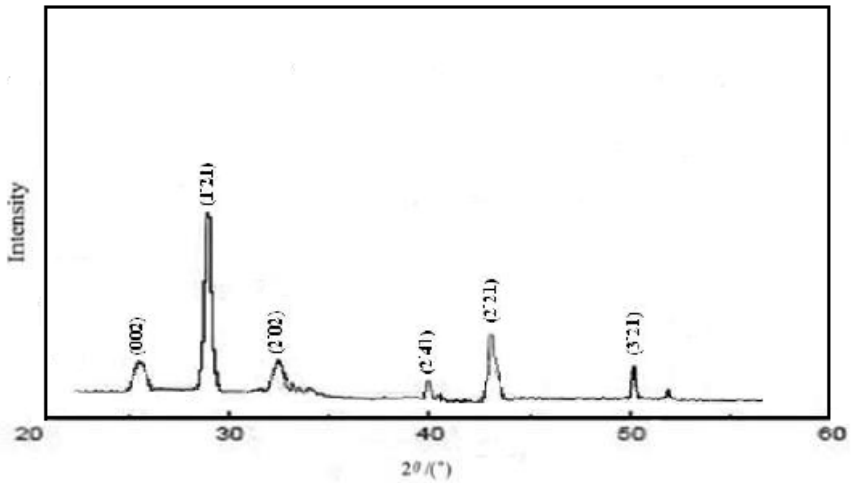

Fig 1. XRD of the bismuth particles calcined at 500 ºC

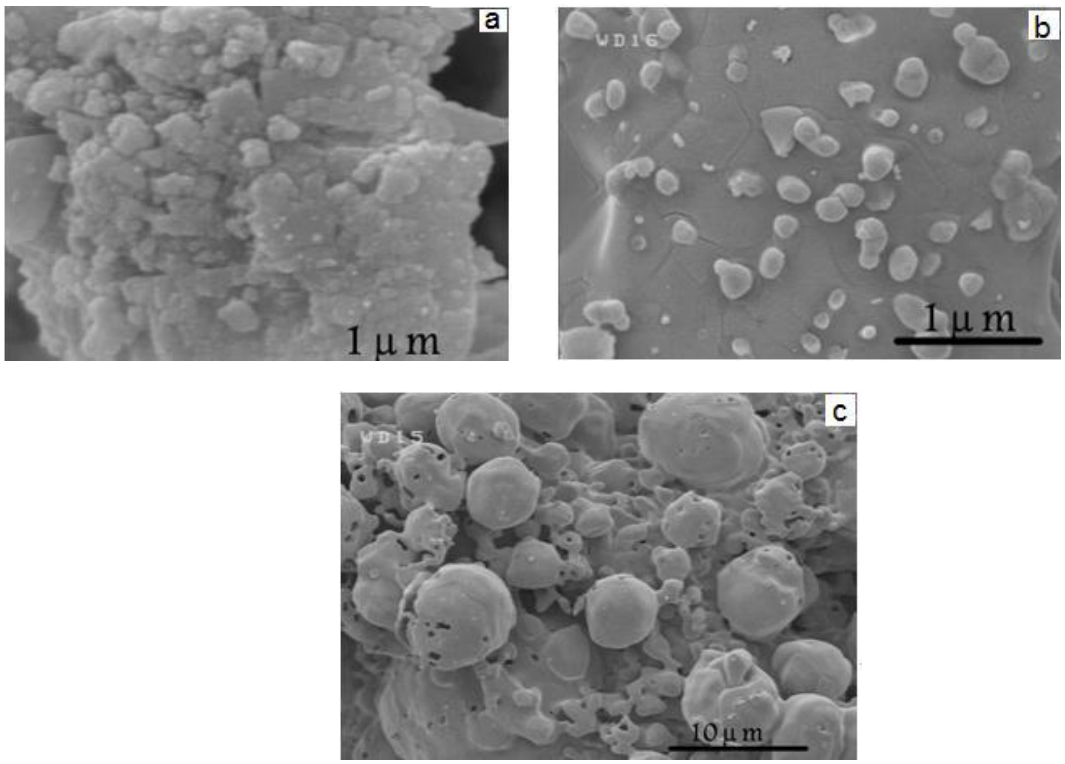

Figure 2. SEM micrographs of thermal treated bismuth particles at (a) 200 ºC (b) 500 ºC (c) 800 ºC

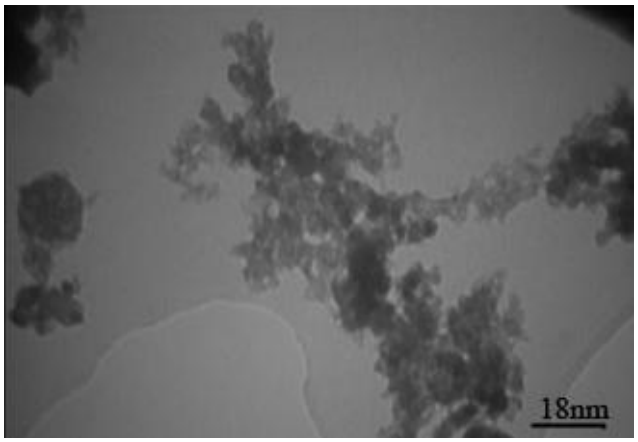

Figure 3. TEM images of the nanoparticles calcined at 500 °C

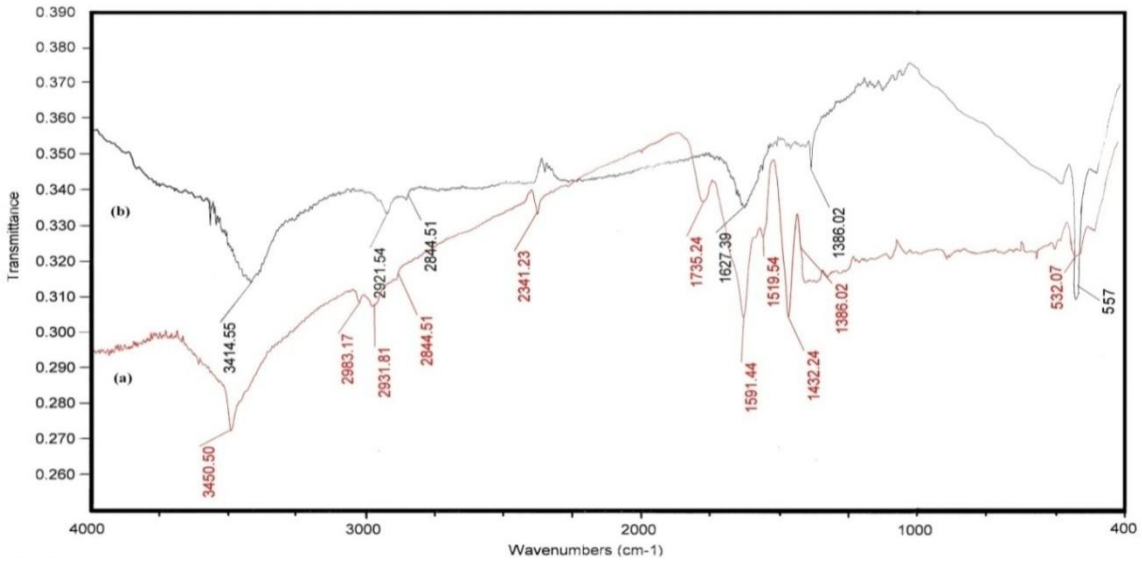

Figure 4. IR spectra of the as-synthesized powders: (a) dried gel at 120°C (b) after calcination at 500°C

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