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Short communication

Synthesis of bismuth oxide nanoparticles by citrate gel method

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Abstract

A mixture of bismuth nitrate and citric acid solution is taken in 1:1 molar ratio and heated on hot water bath. A gel is formed on evaporation of the water, which on decomposition at 400 °C produces nanocrystalline Bi_2O_3 particles. Formation of nanocrystallites of Bi_2O_3 is confirmed by X-ray diffraction (XRD) study. Transmission electron microscope (TEM) investigations revealed that the average particle size is 50 nm for these powders.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; B. X-ray methods

1. Introduction

Bismuth oxide as a component finds use in wide applications in varistors, catalyst and gas sensors. Bismuth oxide (Bi_2O_3)-based compounds are much better solid electrolytes than well-known stabilized zirconia, because the face-centred cubic (fcc) Bi_2O_3 exhibits the highest ion conductivity of all oxide ion conductors [1–3]. Bi_2O_3 is also used as an additive in paints. Furthermore, the total oxidation of isobutene is enhanced on bismuth containing tin catalysts. Typically Bi_2O_3 is prepared via the oxidation of bismuth metal at 800 °C or thermal decomposition of carbonates or hydroxides produced by the addition of alkali-metal hydroxides to bismuth salt solution [4,5]. These powders on calcinations yield fine particles of Bi_2O_3. Flame spray pyrolysis [6] is also used to produce nano-sized Bi_2O_3 particles. The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Using chemical methods, e.g. co-precipitation, sol–gel, hydro-thermal and colloid emulsion technique have been confirmed to efficiently control the morphology and chemical composition of prepared powders. Recently we have reported the synthesis of bismuth oxide nanoparticles by urea method [7]. Here, we report a simple citrate gel process for the preparation of nanocrystalline Bi_2O_3. This method is commonly used for preparation of oxides [8,9] and not yet reported for the preparation of Bi_2O_3 ceramics. This process involves complexation of metal ions by poly functional carboxyl acids, such as citric acid or tartaric acid having one hydroxyl group. On heating this mixture, the solvent (water) evaporates resulting in increased viscosity. On complete removal of water, the mixture is a polymeric gel and its constituents mixed at atomic level. This resin on heating at higher temperature produces the respective oxides.

2. Experimental

Bismuth nitrate and citric acid used for the preparation of Bi_2O_3 are of AR grade. A known quantity of (4 g) $Bi(NO_3)\cdot 5H_2O$ is dissolved in nitric acid [50 ml] and mixed with citric acid in a 1:1 molar ratio and heated on a water bath. Since there was no precipitation during mixing, the pH of the solution was not varied. On heating on a water bath at

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373 K, a yellowish gel was formed after evaporation of water. Subsequently, the gel is decomposed at various temperatures ranging from 423 to 773 K in air. The heating rate employed was 10 K/min and kept for 4 h. 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. Various techniques such as XRD (Philips PW 1710 Diffractometer) and BET surface area measurements (Nova 1200 instrument) were employed to characterize these powders. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10°–80° for a period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. The samples were analyzed for the presence of carbon by microanalysis technique on a CARLO ELBA EA-1108 analyzer.

3. Results and discussion

The citric acid added acts as a complexing agent. The mixture of citric acid and bismuth nitrate solution forms a gel on heating on a water bath which decomposes at higher temperatures >423 K. During calcinations process, a black fluffy mass (foam-like) is formed which occupies large volumes of the furnace. As the temperature increases, the black mass turns to white in colour with the removal of carbon. Samples calcined at 773 K for 20 min shows less than 1% of carbon. At higher temperatures of calcinations, no carbon was found to present. Fig. 1 shows the XRD for the samples heated at 673 K. The sample showed the crystalline pattern and the observed d-lines match the reported values for the β-Bi_2O_3 phase (JCPDS no. 27-50). The calculated lattice parameters by least square fit are $a = 7.736$ Å and $c = 5.614$ Å. The surface area of these oven-dried powders was found to be 90 m^2/g. The average particle size of these powders is found to be 50 nm (Fig. 2). The crystallite size measurements were also carried out (for 102 reflection) using the Scherrer equation, $D = k\lambda/\beta \cos\theta$, where D is the crystallite size, k is a constant (= 0.9 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation, β is the line width (obtained after correction for the instrumental broadening) and θ is the angle of diffraction. The particle size obtained from XRD data is 100 nm.

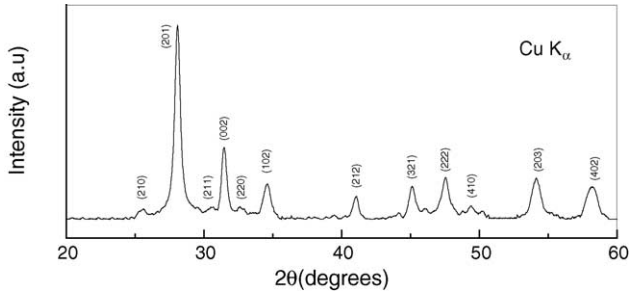

Fig. 1. XRD of Bi_2O_3 powders calcined at 673 K.

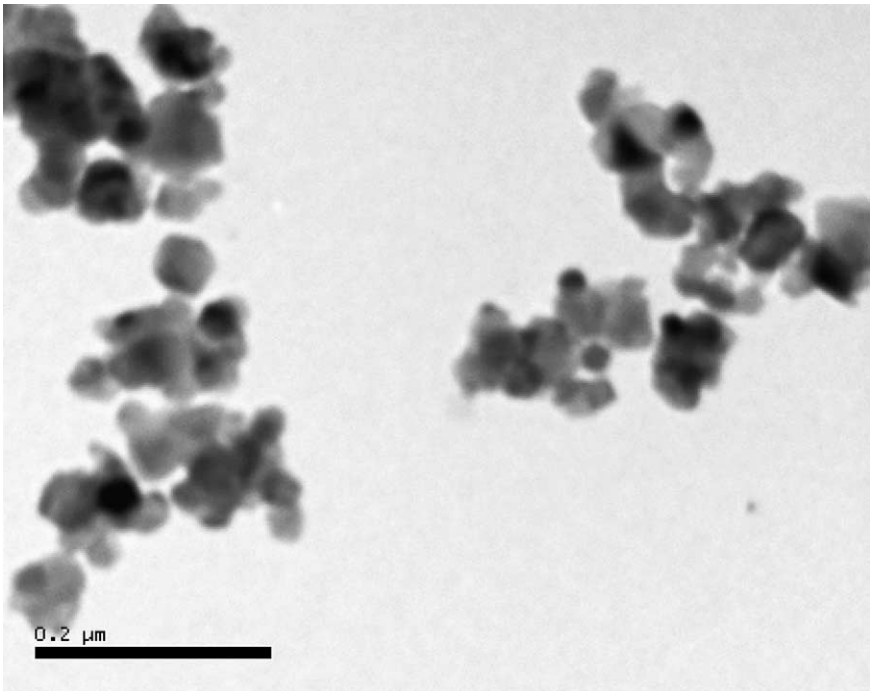

Fig. 2. TEM picture of Bi_2O_3 powders calcined at 673 K.

4. Conclusions

A simple citrate gel process was elucidated to prepare bismuth oxide nanoparticles. The average size of these particles ranges from 50 to 80 nm.

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