# UNIVERSITI PUTRA MALAYSIA

# CHARACTERISATION OF ANTIMONY AND ANTIMONY-BISMUTH OXIDES SYNTHESISED BY PRECIPITATION TECHNIQUE

**NORHAYATI BT MOHD NOOR**

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**By**

**NORHAYATI BT MOHD NOOR**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science**

**April 2007**

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# *Special Dedication To*

| | |
|---|---|
| *My Beloved Husband & Daughter* | *Khairul Affendy Ismail*<br>*Nur Afiqah Irdina* |
| *My Dearest Ma & Abah* | *Hasnah Ismail*<br>*Mohd Noor Salleh* |
| *My Dear Brothers & Sisters* | *Mohd Hilmi*<br>*Mohd Izani*<br>*Mohd Nabil*<br>*Mohd Hanif Ezzat*<br>*Norsyafiqa*<br>*Nor Aliya Auni* |
| *My Dear Parents-in-law* | *Ismail Abd. Rahman*<br>*Shaihah Hamat* |

Thanks to their love and support for all the time no matter what had happened.

*"…. Alhamdulillah"*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

# CHARACTERISATION OF ANTIMONY AND ANTIMONY-BISMUTH OXIDES SYNTHESISED BY PRECIPITATION TECHNIQUE

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**NORHAYATI BINTI MOHD NOOR**

**April 2007**

**Chairman : Associate Professor Dr. Abdul Halim Abdullah, PhD**

**Faculty : Science**

Antimony oxide exists in several different phases and this single oxide has generated considerable interest in applications such as polyethylene terephthalate (PET) production and semiconductor devices manufacturing. In this study, antimony oxide and antimony bismuth oxide have been prepared via precipitation and coprecipitation technique, respectively. The influence of various preparation parameters (starting material, precipitating agent, precipitation route and pH) on the prepared antimony oxide has been investigated. The characteristics of the samples (antimony oxide and antimony bismuth oxide) were determined by Differential Thermogravimetry/Thermogravimetric Analysis (DTG/TGA), Powder X-ray Diffraction Analysis (XRD), Fourier Transform Infrared Analysis (FTIR), Brunauer-Emmett-Teller Surface Area Measurements (BET) and Scanning Electron Microscopy (SEM). Extent of reduction of antimony bismuth oxide was investigated by employing Temperature-Programmed Reduction in $H_2$ (TPR) technique.

Starting material and precipitation route have influenced the formation of the final products which have given the different surface area. By using antimony(III) acetate (raw material) via forward precipitation route, a single phase of $Sb_2O_3$ senarmontite phase with high surface area can be obtained. As the concentration of precipitating agent, NaOH is increased, the formation of antimony oxide phase changed from single phase to mixed phase which was vice versa with increasing of $NH_4OH$ concentration. The sample of high surface area with corresponding ultrafine particle could be achieved at optimum condition (0.6 M of NaOH concentration).

The microstructural change of prepared antimony oxide was determined at various pH values. The pH change does not effect the formation of antimony oxides phases but led to the higher surface area as the pH increases. The evolvement of the antimony bismuth oxide phase occurred as the $NH_4OH$ concentration increases. The high surface area sample with small grain size can be obtained using 0.6 M $NH_4OH$. This sample gave small amount of oxygen removal in accordance to TPR result.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai
memenuhi keperluan untuk ijazah Master Sains

# PENCIRIAN ANTIMONI DAN ANTIMONI-BISMUT OKSIDA YANG DISINTESIS MENGGUNAKAN TEKNIK PEMENDAKAN

Oleh

**NORHAYATI BINTI MOHD NOOR**

**April 2007**

**Pengerusi : Professor Madya Dr. Abdul Halim Abdullah, PhD**

**Fakulti : Sains**

Antimoni oksida wujud di dalam beberapa fasa yang berlainan dan oksida tunggal ini telah mendapat perhatian di dalam pengaplikasian seperti penghasilan polietilena taraftalat (PET) dan pembuatan peranti semikonduktor. Di dalam kajian ini, antimoni oksida dan antimoni bismut oksida telah disediakan melalui teknik pemendakan dan kopemendakan. Kesan pelbagai parameter penyediaan (bahan pemula, agen pemendakan, arah pemendakan dan pH) ke atas antimoni oksida yang disediakan telah dikaji. Ciri-ciri bagi sampel antimoni oksida dan antimoni bismut oksida telah ditentukan dengan menggunakan Analisis Termogravimetri (DTG/TGA), Analisis Pembelauan X-ray (XRD), Analisis Spektroskopi Sinarmerah (FTIR), Pengukuran Luas Permukaan dengan kaedah BET dan Mikroskopi Pengimbas Elektron (SEM). Penurunan antimoni bismut oksida dikaji dengan menjalankan ujikaji Penurunan Berprogram Suhu (TPR).

Bahan pemula dan arah pemendakan telah mempengaruhi pembentukan hasil di mana ia telah memberikan luas permukaan yang berbeza. Dengan menggunakan antimoni triasetat sebagai bahan pemula melalui teknik pemendakan secara ke hadapan, fasa tunggal iaitu $Sb_2O_3$ fasa senarmontite yang mempunyai luas permukaan yang besar boleh dicapai. Bagi kajian kesan agen presipitasi; apabila kepekatan NaOH meningkat, pembentukan fasa antimoni oksida berubah daripada fasa tunggal kepada fasa campuran di mana keadaan sebaliknya berlaku apabila kepekatan $NH_4OH$ ditingkatkan. Sampel dengan luas permukaan yang tinggi dan partikel yang halus boleh dicapai pada keadaan optimum (kepekatan NaOH adalah 0.6 M).

Perubahan struktur mikro pada antimoni oksida yang disediakan telah ditentukan pada pelbagai pH. Pembentukan fasa antimoni oksida tidak dipengaruhi oleh perubahan pH tetapi cenderung memberikan luas permukaan yang tinggi apabila pH ditingkatkan. Perkembangan fasa antimoni bismus oksida berlaku apabila kepekatan $NH_4OH$ meningkat. Sampel yang mempunyai luas permukaan yang tinggi dan bersaiz butiran kecil boleh dihasilkan pada $NH_4OH$ berkepekatan 0.6 M. Sampel ini memberikan amaun penyingkiran oksigen yang rendah berdasarkan keputusan TPR.

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*Bismillahirrahmanirrahim…*

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Last but not least, thanks to all those who had contributed to the success of this work in one way or another especially my beloved husband, daughter, parents, sisters, brothers and parents-in-law for being supportive and understanding.

Financial support from University Putra Malaysia and the Ministry of Science, Technology and Innovation in the form of PASCA Graduate scheme is gratefully acknowledged.

I certify an Examination Committee met on 13th April 2007 to conduct the final examination of Norhayati Binti Mohd Noor on her Master of Science thesis entitled "Characterisation of Antimony and Antimony-Bismuth Oxides Synthesised by Precipitation Technique" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) regulations 1981. The Committee recommends that the student be awarded the degree of Master of Science.

Members of the Examination Committee were as follows:

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Date: 13 November 2007

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirements for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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Date:

# DECLARATION

I hereby declare that the thesis is based on my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

**NORHAYATI BINTI MOHD NOOR**

Date:

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| BET | Brunauer-Emmett-Teller |
| Bi | Bismuth |
| FTIR | Fourier Transform Infrared Spectroscopy |
| FWHM | Full-Width at Half Maximum |
| JCPDS | Joint Committee on Powder Diffraction Standards |
| PET | Polyethylene Terephthalate |
| SEM | Scanning Electron Microscopy |
| SOHIO | Standard Oil Company of Ohio |
| TGA | Thermogravimetric Analysis |
| TPR | Temperature Programmed Reduction |
| XRD | X-ray Diffraction |

# CHAPTER 1

# GENERAL INTRODUCTION

## 1.1 Antimony Oxide

Antimony exists in the oxidation states of -3, 0, +3 and +5. There are a few phases in oxide of antimony which exist in several different compositions and display polymorphism. $Sb_2O_3$, $Sb_2O_4$, $Sb_2O_5$ and $Sb_6O_{13}$ are the common phases of antimony oxide. Golunski *et al.* [1] claimed that phase studies of the antimony-oxygen system have often been complicated by the following factors (a) the oxides tend to exhibit allotropy; (b) both Sb(III) and Sb(V) ions can be present in oxides of different stoichiometries; and (c) the evolution of water from hydrated precursors does not necessarily yield the expected anhydrous oxides.

The research on Sb-O composition and structure by many researchers has been summarized. Antimony trioxide exists in two crystal structures, cubic and orthorhombic both of which are stable at room temperature [2, 3]. Cubic $Sb_2O_3$, also known as senarmontite, has a structure based on $Sb_4O_6$ molecule [1, 4, 5]. This crystal was stable below 843 K [6] and can exist as molecules in the gas phase [2]. Meanwhile, orthorhombic $Sb_2O_3$, also known as valentinite, has a layered structure, in which long chains (each "link"contains three $O^{2-}$ ions and shares four $Sb^{3+}$ ions) are held together by weak Sb-O interactions [5].

When heating senarmontite in the absence of oxygen, the first thermal effect to be observed is usually the onset of sublimation at ca. 775 K. Senarmontite is transformed to valentinite, at about 829 K with a melting point of 929 K [7, 8]. Finely ground valentinite has also been reported to oxidize at a lower temperature than senarmontite [2, 3]. In addition, Trofimov *et al.* [9] found that mixtures of senarmontite and valentinite do not oxidize additively. In their work, when finely divided senarmontite was oxidized in air, orthorhombic $Sb_2O_4$ also known as cervantite, was produced at 733 K. Under similar conditions, valentinite oxidized at 673 K. The oxidation of orthorhombic valentinite $Sb_2O_3$ to orthorhombic cervantite $Sb_2O_4$ as well as the reverse reduction is a topotactic reaction, where the structure of valentinite is completely preserved in cervantite.

The oxidation involves very little change in the structure of valentinite, and the additional oxygen atoms in cervantite merely occupy positions along the empty channels present in the former. The mechanism has been proposed whereby the diffusion of oxygen atoms involving the making and breaking of bonds between (pentavalent) antimony and these oxygen atoms. The additional oxygen atoms in cervantite occupy positions along the empty channels available in the structure of valentinite and bridge the $(Sb_2O_3)_\infty$ chains in the direction a perpendicular to the length of the channels [10]. Molten $Sb_2O_3$ is very volatile between 925 and 1125 K, but it loses mass more slowly at higher temperatures [2, 3]. It seems probable that, on melting, valentinite forms a mobile liquid consisting of $Sb_4O_6$ molecules, which then associates to form polymeric Sb-O chains [2] and thus yields a much more viscous liquid phase. All the observations suggested that sublimation is critical in the oxidation of $Sb_2O_3$ [7].

In common with other elements in the B subgroups of the Periodic Table, antimony has a tendency to form mixed-valent compounds in which the two oxidation states may be represented by *N* and *N*-2 (where *N* is the principal state for the group) [1]. In $Sb_2O_4$, the Sb(V) and Sb(III) ions are present in equal proportions [1, 11]. Therefore, the fact that some commercial samples are listed as “antimony(IV) oxide” can only be justified as a way of indicating the mean oxidation state of the metal ions, and so distinguishing the tetroxide from $Sb_6O_{13}$. There are two polymorphic forms of $Sb_2O_4$ *i. e.* orthorhombic α-phase (cervantite) and a high-temperature monoclinic β-phase [1]. According to Xiong *et al.* [12], pure α-$Sb_2O_4$ is inactive and inert.

Figure 1.1 (a) and (b) show a molecular structure of α-$Sb_2O_4$ and β-$Sb_2O_4$. The α-$Sb_2O_4$ structure is similar to the β structure, but of a lower symmetry. A major difference between α and β forms is in the coordination of the $Sb^{3+}$ ions. In the β structure four oxygen atoms are within bonding distance, whereas in α structure a fifth oxygen atom comes within bonding distance [13].

Between the two, the orthorhombic α-form (cervantite) [1, 14 and 15] is the more common; it is the usual product of the oxidation of $Sb_2O_3$ under air/oxygen, and of the decomposition of some of the higher oxides such as $Sb_2O_5.nH_2O$ [2] or $Sb_6O_{13}$ [2, 16]. Cervantite is remarkably stable and is found not to undergo any physical or chemical change on heating below 1273 K, either in air or nitrogen [2, 3]. Above 1273 K, an endothermic process occurs [3], leading to a complete loss of mass. One possibility is that cervantite sublimes at high temperatures [2]. Accordingly, it has been proposed that cervantite decomposes to yield oxygen and $Sb_2O_3$, which immediately melts and volatilizes [3]:

$$\alpha\text{-}Sb_2O_4\,(s) \longrightarrow \tfrac{1}{2}O_2\,(g) + Sb_2O_3\,(s) \qquad (1)$$

$$Sb_2O_3\,(s) \longrightarrow [Sb_2O_3\,(l)] \longrightarrow \tfrac{1}{2}Sb_4O_6\,(g) \qquad (2)$$

Rogers and Skapski, quoted by Golunski [1], have suggested the following route for the transformation of $\alpha$-$Sb_2O_4$ to the monoclinic $\beta$-form:

$$2\alpha\text{-}Sb_2O_4\,(s) \longrightarrow Sb_4O_6\,(g) + O_2 \rightleftharpoons 2\beta\text{-}Sb_2O_4\,(s) \qquad (3)$$

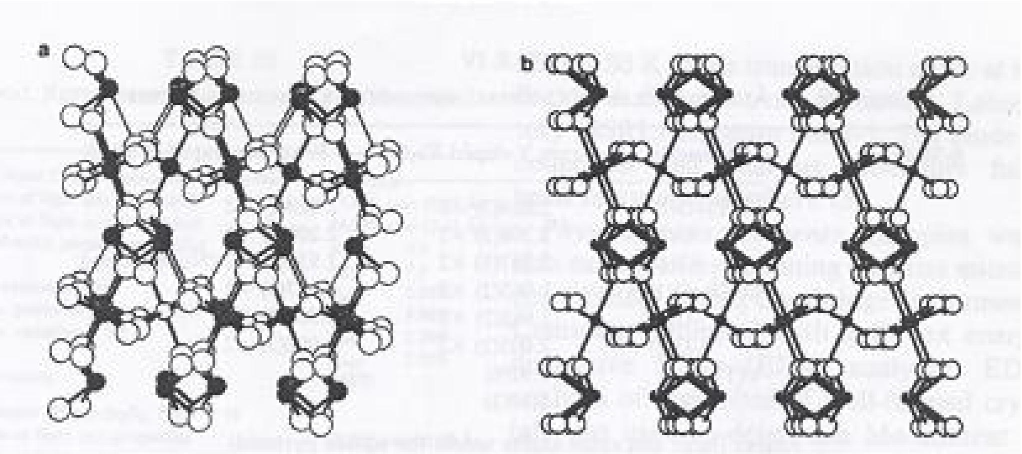

Figure 1.1: (a) $\alpha$-antimony oxide ($\alpha$-$Sb_2O_4$). (b) $\beta$-antimony oxide ($\beta$-$Sb_2O_4$). Filled spheres represent Sb atoms; open spheres, oxygen atoms. Note the two kinds of coordination for the two types of Sb atoms. $Sb^{5+}$ atoms are octahedrally coordinated. The asymmetric coordination of the $Sb^{3+}$ is due to the presence of a lone electron pair; these form channels of electron density perpendicular to the views presented here. These Sb atoms are four-coordinate in the $\beta$ form. In $\alpha$ form, fifth oxygen is weakly bonded to $Sb^{3+}$. There are two types of oxygen atoms in $\beta$-$Sb_2O_4$, one type bridges $Sb^{5+}$ atoms only, while the second type bridges $Sb^{3+}$ and $Sb^{5+}$ atoms [13].

Under high pressure, the oxidation of the tetroxide [1] becomes more likely than its dissociation. Golunski *et al.* [1] suggested that the following sequence may, therefore apply:

$$\alpha\text{-}Sb_2O_4 + ½O_2 \rightleftharpoons \underset{\text{(antimony(V) oxide)}}{Sb_2O_5} \longrightarrow \beta\text{-}Sb_2O_4 + ½O_2 \qquad (4)$$

The most common hydrated form of antimony(V) oxide (antimonic acid) has a pyrochlore-type structure [1, 17], in which anion vacancies may be occupied by oxygen atoms from the water molecules [1]. Olen'kova, quoted by Golunski, [1] also predicted that the maximum value of $n$ should be 3 in $Sb_2O_5.nH_2O$, though this value is often exceeded. On heating $Sb_2O_5.nH_2O$ to 1273 K, most of the mass is lost below 1125 K [2]. The loss occurs in two stages where the first stage (350-475 K) is due to partial dehydration; while the second (925-1125 K) is the result of concurrent evolution of water of crystallization and of lattice oxygen, with the resultant formation of $Sb_6O_{13}$ [2]. Cubic $Sb_2O_5$ loses oxygen progressively on heating above 673 K, leading eventually to the formation of orthorhombic $Sb_2O_4$ [3]. Anhydrous antimony(V) oxide cannot be prepared directly from $Sb_2O_5.nH_2O$ [1, 2].

The final antimony oxide that exists is $Sb_6O_{13}$ which can be considered as intermediate phase between $Sb_2O_5$ and $Sb_2O_3$ in terms of both structure [1] and thermal stability [2]. There are several reasons why $Sb_6O_{13}$ can be mistakenly identified as $Sb_2O_5$, but it seems that the original cause was the widespread belief that $Sb_2O_5$ could be prepared by heating $Sb_2O_5.nH_2O$ until no further water was evolved.

## 1.2 Preparation of Antimony Oxide

### 1.2.1 Preparation Methods

The material properties are strongly affected by every step of the preparation together with the quality of the raw materials. The choice of a laboratory preparation of a given material depends on the physical and chemical characteristics desired in the final composition [18]. Nowadays, many methods and techniques have been discovered by researchers in order to synthesize the mono and mixed metal oxide systems with the best performance, which is very useful in industry.

Recently, however, to our knowledge, only a few studies on synthesis of the antimony oxide and its characteristics have been reported [19, 20]. This oxide can be readily synthesized with various well-develop techniques such as thermal vapor condensation [21, 22], hydrothermal method [20, 23] and sol-gel method [23, 24]. There are however some problems and limitations, such as complex technique, limited success with refractory metal for the gas condensation, high temperature and high pressure for the hydrothermal method [23]. Beside the weakness of the thermal vapor condensation, this method is considered to be the most appropriate for the production of nonagglomerated nanoparticles with clean surface [22]. The antimony trioxide was successfully synthesized under controlled atmosphere using the γ-ray radiation-oxidation route method or chemical method [19, 23]. Recently, scientists have developed a new method using the hybrid induction and laser heating (HILH) method. This method was claimed