UNIVERSITI PUTRA MALAYSIA

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

NORHAYATI BT MOHD NOOR

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

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

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>vii</td>
</tr>
<tr>
<td>APPROVAL</td>
<td>viii</td>
</tr>
<tr>
<td>DECLARATION</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xviii</td>
</tr>
</tbody>
</table>

## CHAPTER

### 1 GENERAL INTRODUCTION
1.1 Antimony Oxide 1
1.2 Preparation of Antimony Oxide 6
   1.2.1 Preparation Methods 6
   1.2.2 Effects of Preparation Parameters 9
1.3 Industrial Application of Antimony Oxide 14
   1.3.1 The Role of Antimony Oxide as a Mixed Oxide Catalysts 15
1.4 Bismuth Oxide 20
1.5 Objectives of the Study 22

### 2 METHODOLOGY
2.1 Materials and Gases 23
2.2 Preparation of Antimony Oxide via Different Preparation Parameters 24
   2.2.1 Starting Material, Precipitation Route, Precipitating Agent and pH 24
2.3 Preparation of Antimony-Bismuth Oxide via Coprecipitation Method 26
2.4 Characterizations 27
   2.4.1 Differential Thermogravimetry/Thermogravimetric Analysis (DTG/TGA) 27
   2.4.2 Powder X-ray Diffraction (XRD) 27
   2.4.3 Fourier Transform Infrared (FT-IR) Spectroscopy 28
   2.4.4 BET Surface Area Measurements 28
   2.4.5 Scanning Electron Microscopy (SEM) 29
   2.4.6 Temperature-Programmed Reduction (TPR) in H₂ 29
3 RESULTS AND DISCUSSION

3.1 Effect of Precipitation Route on Antimony Oxide Properties

3.1.1 Titration Curve and Yield of Antimony Oxide

3.1.2 Differential Thermogravimetry/Thermogravimetric Analysis (DTG/TGA)

3.1.3 Phase Identification using Powder XRD Technique

3.1.4 Fourier Transform Infrared (FT-IR) Spectroscopy

3.1.5 BET Surface Area Measurements

3.1.6 Scanning Electron Microscopy (SEM)

3.1.7 Conclusion

3.2 Effect of Precipitating Agent Concentration on Antimony Oxide Properties

3.2.1 Effect of Precipitating Agent Concentration: NaOH as a Precipitating Agent

3.2.2 Effect of Precipitating Agent Concentration: NH₄OH as a Precipitating Agent

3.3 Effect of pH by using NaOH Solution as a Precipitating Agent and Antimony(III) Acetate as a Salt Solution

3.3.1 Titration Curve and Yield of Antimony Oxide

3.3.2 Phase Identification using Powder XRD Technique

3.3.3 Fourier Transform Infrared (FT-IR) Spectroscopy

3.3.4 BET Surface Area Measurements

3.3.5 Scanning Electron Microscopy (SEM)

3.3.6 Conclusion

3.4 Preparation of Antimony-Bismuth Oxides

3.4.1 Titration Curve and Yield of Antimony-Bismuth Oxide

3.4.2 Thermogravimetric Analysis (TGA)

3.4.3 Phase Identification using Powder XRD Technique

3.4.4 Fourier Transform Infrared (FT-IR) Spectroscopy

3.4.5 BET Surface Area Measurements

3.4.6 Scanning Electron Microscopy (SEM)

3.4.7 Temperature-Programmed Reduction (TPR) in H₂

3.4.8 Conclusion

4 SUMMARY AND CONCLUDING REMARKS

REFERENCES
APPENDICES
BIODATA OF THE AUTHOR
Special Dedication To

My Beloved Husband & Daughter
Khairul Affendy Ismail
Nur Afiqah Irdina

My Dearest Ma & Abah
Hasnah Ismail
Mohd Noor Salleh

My Dear Brothers & Sisters
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Mohd Hanif Ezzat
Norsyafiqqa
Nor Aliya Auni

My Dear Parents-in-law
Ismail Abd. Rahman
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

By

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 H₂ (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 Sb₂O₃ 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 NH₄OH 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 NH₄OH concentration increases. The high surface area sample with small grain size can be obtained using 0.6 M NH₄OH. 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

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 Sb₂O₃ 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 NH₄OH 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 NH₄OH meningkat. Sampel yang mempunyai luas permukaan yang tinggi dan bersaiz butiran kecil boleh dihasilkan pada NH₄OH berkepekatan 0.6 M. Sampel ini memberikan amaun penyingkiran oksigen yang rendah berdasarkan keputusan TPR.
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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.

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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:
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Percentage Yield of FSb, RSb, FKSb and RKSb samples before calcination</td>
<td>33</td>
</tr>
<tr>
<td>3.2</td>
<td>$2\theta$ and d values of uncalcined and calcined RKSb sample</td>
<td>40</td>
</tr>
<tr>
<td>3.3</td>
<td>Crystallite sizes of FSb, RSb, FKSb and RKSb samples</td>
<td>40</td>
</tr>
<tr>
<td>3.4</td>
<td>Grain sizes of FSb, RSb, FKSb and RKSb samples</td>
<td>44</td>
</tr>
<tr>
<td>3.5</td>
<td>Percentage yield of 01Sb, 02Sb, 04Sb, 06Sb, 08Sb and 10Sb samples before calcination</td>
<td>51</td>
</tr>
<tr>
<td>3.6</td>
<td>Crystallite sizes of (a) 01Sb, (b) 02Sb, (c) 04Sb, (d) 06Sb, (e) 08Sb and (f) 10Sb samples</td>
<td>52</td>
</tr>
<tr>
<td>3.7</td>
<td>Grain sizes of (a) 01Sb, (b) 02Sb, (c) 04Sb, (d) 06Sb, (e) 08Sb and (f) 10Sb samples</td>
<td>56</td>
</tr>
<tr>
<td>3.8</td>
<td>Percentage yield of 01SbN, 02SbN, 04SbN, 06SbN, 08SbN and 10SbN samples before calcination</td>
<td>63</td>
</tr>
<tr>
<td>3.9</td>
<td>Crystallite sizes of (a) 01SbN, (b) 02SbN, (c) 04SbN, (d) 06SbN, (e) 08SbN and (f) 10SbN samples</td>
<td>67</td>
</tr>
<tr>
<td>3.10</td>
<td>Grain sizes of (a) 01SbN, (b) 02SbN, (c) 04SbN, (d) 06SbN, (e) 08SbN and (f) 10SbN samples</td>
<td>70</td>
</tr>
<tr>
<td>3.11</td>
<td>Percentage yield of pH5Sb, pH9Sb and pH11Sb samples before calcination</td>
<td>78</td>
</tr>
<tr>
<td>3.12</td>
<td>Crystallite sizes of (a) pH5Sb, (b) pH9Sb and (c) pH11Sb samples</td>
<td>79</td>
</tr>
</tbody>
</table>
3.13 Grain sizes of (a) pH5Sb, (b) pH9Sb and (c) pH11Sb samples 83
3.14 Percentage yield of SB1, SB2 and SB3 samples before calcination 90
3.15 Crystallite sizes of (a) SB1, (b) SB2 and (c) SB3 samples 95
3.16 Grain sizes of (a) SB1, (b) SB2 and (c) SB3 samples 98
3.17 Total amount of oxygen atoms removed from SB2 sample 102
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Molecular structure of $\alpha$-Sb$_2$O$_4$ and $\beta$-Sb$_2$O$_4$</td>
<td>4</td>
</tr>
<tr>
<td>3.1 Titration curves of (a) FKSb, (b) FSb, (c) RSb and (d) RKSB samples</td>
<td>31</td>
</tr>
<tr>
<td>3.2 Thermogram of (a) antimony(III) acetate, (b) antimony potassium tartarate and (c) prepared antimony oxides</td>
<td>34</td>
</tr>
<tr>
<td>3.3 Thermogram of uncalcined FSb sample</td>
<td>35</td>
</tr>
<tr>
<td>3.4 Thermogram of calcined (a) RKSB, (b) FKSb, (c) RSb and FSb samples</td>
<td>36</td>
</tr>
<tr>
<td>3.5 XRD patterns of calcined (a) FSb, (b) RSb, (c) FKSb and (d) RKSB samples</td>
<td>38</td>
</tr>
<tr>
<td>3.6 FTIR spectrums of calcined (a) FSb, (b) RSb, (c) FKSb and (d) RKSB samples</td>
<td>42</td>
</tr>
<tr>
<td>3.7 BET surface area measurement of calcined (a) FSb, (b) RSb, (c) FKSb and (d) RKSB samples</td>
<td>44</td>
</tr>
<tr>
<td>3.8 (a) SEM micrograph of FSb sample</td>
<td>45</td>
</tr>
<tr>
<td>(b) SEM micrograph of RSb sample</td>
<td>46</td>
</tr>
<tr>
<td>(c) SEM micrograph of FKSb sample</td>
<td>46</td>
</tr>
<tr>
<td>(d) SEM micrograph of RKSB sample</td>
<td>47</td>
</tr>
<tr>
<td>3.9 Titration curves of (a) 01Sb, (b) 02Sb, (c) 04Sb, (d) 06Sb, (e) 08Sb and (f) 10Sb samples</td>
<td>49</td>
</tr>
<tr>
<td>3.10 XRD patterns of calcined (a) 01Sb, (b) 02Sb, (c) 04Sb, (d) 06Sb, (e) 08Sb and (f) 10Sb samples</td>
<td>53</td>
</tr>
</tbody>
</table>
3.11 FTIR spectrums of (a) 01Sb, (b) 02Sb, (c) 04Sb, (d) 06Sb, (e) 08Sb and (f) 10Sb samples

3.12 BET surface area measurement of calcined (a) 01Sb, (b) 02Sb, (c) 04Sb, (d) 06Sb, (e) 08Sb and (f) 10Sb samples

3.13 (a) SEM micrograph of 01Sb sample
(b) SEM micrograph of 02Sb sample
(c) SEM micrograph of 04Sb sample
(d) SEM micrograph of 06Sb sample
(e) SEM micrograph of 08Sb sample
(f) SEM micrograph of 10Sb sample

3.14 Titration curves of (a) 01SbN, (b) 02SbN, (c) 04SbN, (d) 06SbN, (e) 08SbN and (f) 10SbN samples

3.15 XRD patterns of uncalcined (a) 01SbN, (b) 02SbN, (c) 04SbN, (d) 06SbN, (e) 08SbN and (f) 10SbN samples

3.16 XRD patterns of calcined (a) 01SbN, (b) 02SbN, (c) 04SbN, (d) 06SbN, (e) 08SbN and (f) 10SbN samples

3.17 FTIR spectrums of calcined (a) 01SbN, (b) 02SbN, (c) 04SbN, (d) 06SbN, (e) 08SbN and (f) 10SbN samples

3.18 BET surface area measurement of calcined (a) 01SbN, (b) 02SbN, (c) 04SbN, (d) 06SbN, (e) 08SbN and (f) 10SbN samples

3.19 (a) SEM micrograph of 01SbN sample
(b) SEM micrograph of 02SbN sample
(c) SEM micrograph of 04SbN sample
(d) SEM micrograph of 06SbN sample
(e) SEM micrograph of 08SbN sample 74
(f) SEM micrograph of 10SbN sample 74

3.20  Titration curves of (a) pH5Sb, (b) pH9Sb and (c) pH11Sb samples 77

3.21  XRD patterns of calcined (a) pH5Sb, (b) pH9Sb and (c) pH11Sb samples 80

3.22  FTIR spectrums of calcined (a) pH5Sb, (b) pH9Sb and (c) pH11Sb samples 82

3.23  BET surface area measurement of calcined (a) pH5Sb, (b) pH9Sb and (c) pH11Sb samples 83

3.24  (a) SEM micrograph of pH5Sb sample 84
(b) SEM micrograph of pH9Sb sample 85
c) SEM micrograph of pH11Sb sample 85

3.25  Titration curves of (a) SB1, (b) SB2 and (c) SB3 samples 88

3.26  Thermogram of uncalcined (a) SB1, (b) SB2 and (c) SB3 samples 91

3.27  XRD patterns of calcined (a) SB1, (b) SB2 and (c) SB3 samples 93

3.28  FTIR spectrums of calcined (a) SB1, (b) SB2 and (c) SB3 samples 96

3.29  BET surface area measurement of calcined (a) SB1, (b) SB2 and (c) SB3 samples 97

3.30  (a) SEM micrograph of SB1 sample 98
(b) SEM micrograph of SB2 sample 99
c) SEM micrograph of SB3 sample 99

3.31  H2-TPR spectra of SB2 sample 101
LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>Bi</td>
<td>Bismuth</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width at Half Maximum</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene Terephthalate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SOHIO</td>
<td>Standard Oil Company of Ohio</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
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$_2$O$_3$, Sb$_2$O$_4$, Sb$_2$O$_5$ and Sb$_6$O$_{13}$ 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$_2$O$_3$, also known as senarmontite, has a structure based on Sb$_4$O$_6$ 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$_2$O$_3$, 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$_2$O$_4$ also known as cervantite, was produced at 733 K. Under similar conditions, valentinite oxidized at 673 K. The oxidation of orthorhombic valentinite Sb$_2$O$_3$ to orthorhombic cervantite Sb$_2$O$_4$ 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$_2$O$_3$)$_x$ chains in the direction a perpendicular to the length of the channels [10]. Molten Sb$_2$O$_3$ 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$_4$O$_6$ 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$_2$O$_3$ [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\(_2\)O\(_4\), 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\(_6\)O\(_{13}\). There are two polymorphic forms of Sb\(_2\)O\(_4\) i.e. orthorhombic \( \alpha \)-phase (cervantite) and a high-temperature monoclinic \( \beta \)-phase [1]. According to Xiong et al. [12], pure \( \alpha \)-Sb\(_2\)O\(_4\) is inactive and inert.

Figure 1.1 (a) and (b) show a molecular structure of \( \alpha \)-Sb\(_2\)O\(_4\) and \( \beta \)-Sb\(_2\)O\(_4\). The \( \alpha \)-Sb\(_2\)O\(_4\) structure is similar to the \( \beta \) structure, but of a lower symmetry. A major difference between \( \alpha \) and \( \beta \) forms is in the coordination of the Sb\(^{3+}\) ions. In the \( \beta \) structure four oxygen atoms are within bonding distance, whereas in \( \alpha \) structure a fifth oxygen atom comes within bonding distance [13].

Between the two, the orthorhombic \( \alpha \)-form (cervantite) [1, 14 and 15] is the more common; it is the usual product of the oxidation of Sb\(_2\)O\(_3\) under air/oxygen, and of the decomposition of some of the higher oxides such as Sb\(_2\)O\(_5\)\(\cdot\)nH\(_2\)O [2] or Sb\(_6\)O\(_{13}\) [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 \( \text{Sb}_2\text{O}_3 \), which immediately melts and volatilizes \([3]\):

\[
\alpha\text{-Sb}_2\text{O}_4 (s) \rightarrow \frac{1}{2}\text{O}_2 (g) + \text{Sb}_2\text{O}_3 (s) \quad (1)
\]

\[
\text{Sb}_2\text{O}_3 (s) \rightarrow [\text{Sb}_2\text{O}_3 (l)] \rightarrow \frac{1}{2}\text{Sb}_4\text{O}_6 (g) \quad (2)
\]

Rogers and Skapski, quoted by Golunski \([1]\), have suggested the following route for the transformation of \( \alpha\text{-Sb}_2\text{O}_4 \) to the monoclinic \( \beta \)-form:

\[
2\alpha\text{-Sb}_2\text{O}_4 (s) \rightarrow \text{Sb}_4\text{O}_6 (g) + \text{O}_2 \iff 2\beta\text{-Sb}_2\text{O}_4 (s) \quad (3)
\]

**Figure 1.1:** (a) \( \alpha \)-antimony oxide \((\alpha\text{-Sb}_2\text{O}_4)\). (b) \( \beta \)-antimony oxide \((\beta\text{-Sb}_2\text{O}_4)\).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 \( \beta\text{-Sb}_2\text{O}_4 \), 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:

\[
\alpha\text{-Sb}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Sb}_2\text{O}_5 \rightarrow \beta\text{-Sb}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \\
\text{(antimony(V) oxide)}
\]

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\(_2\)O\(_n\).\text{H}_2\text{O}, though this value is often exceeded. On heating Sb\(_2\)O\(_n\).\text{H}_2\text{O} 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\(_6\)O\(_{13}\) [2]. Cubic Sb\(_2\)O\(_5\) loses oxygen progressively on heating above 673 K, leading eventually to the formation of orthorhombic Sb\(_2\)O\(_4\) [3]. Anhydrous antimony(V) oxide cannot be prepared directly from Sb\(_2\)O\(_n\).\text{H}_2\text{O} [1, 2].

The final antimony oxide that exists is Sb\(_6\)O\(_{13}\) which can be considered as intermediate phase between Sb\(_2\)O\(_5\) and Sb\(_2\)O\(_3\) in terms of both structure [1] and thermal stability [2]. There are several reasons why Sb\(_6\)O\(_{13}\) can be mistakenly identified as Sb\(_2\)O\(_5\), but it seems that the original cause was the widespread belief that Sb\(_2\)O\(_5\) could be prepared by heating Sb\(_2\)O\(_n\).\text{H}_2\text{O} 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 $\gamma$-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