Facile Synthesis of Copper Antimonite

Running Title: Synthesis of Copper Antimonite

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Abstract Copper antimonite, $CuSb_2O_4$, is a candidate oxidant for use in time delays for mining detonators. A facile process for the synthesis of copper antimonite comprises the reaction of antimony trioxide with copper-ammonia complex with excess ammonia at reflux conditions (ca. 65 °C) for about 1 h. Thereafter the reaction is driven to completion by driving off the ammonia by distillation. A well-crystallized product with a cuboid crystal habit approximately 4 µm in size is obtained.

Keywords Synthesis, Copper antimonite, Pyrotechnic, Time delay

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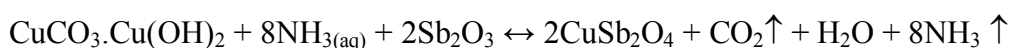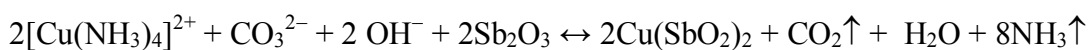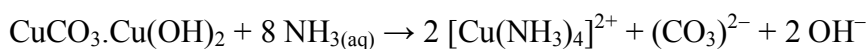
Introduction

The existence of the compounds $CuSb_2O_6$, $Cu_9Sb_4O_{19}$, $Cu_4SbO_{4.5}$ and Cu_5SbO_6 are well-established in the ternary copper-antimony-oxygen system and all can be prepared by solid state reactions (Shimada *et al*., 1985; Shimada *et al*., 1988; Shimada *et al*., 1989; Nakua *et*

al., 1991; Stan *et al*., 1998; Kol'tsova and Chastukhin, 2002; Rey *et al*., 2011). None of these studies reported the formation of copper antimonite ($CuSb_2O_4$) and this suggests that this compound is not accessible via this route. This green crystalline compound compound is mentioned by Mellor (1933). It is a candidate oxidant for use in time delays for mining detonators (Ricco *et al*., 2004) as, unlike some other systems, formulations are possible that can be ignited using a shock tube alone.

Copper antimonite can be prepared by adding a dilute solution of copper(II)sulfate to a suspension of antimony trioxide in a sodium hydroxide solution (Mellor, 1933; Ricco et al., 2004). However, this process requires very careful pH control to avoid side reactions and it also generates a sodium sulfate-containing effluent. The objective of this investigation was to find a robust synthesis route for $CuSb_2O_4$ that would generate a minimum of waste. Towards this end the reactions shown in Scheme I were considered. In the first step the copper ammonia complex is formed by contacting copper hydroxide carbonate with ammonia solution to form Schweitzer's reagent (Schweizer, 1857; Kauffman, 1984). Next this tetraammine-copper complex is allowed to react with suspended a solid antimony trioxide powder. The net reaction shows that the ammonia reagent is released as a vapour that can be recovered and recycled for reuse.

Scheme I. Reaction sequence

$$CuCO_3.Cu(OH)_2 + 8\ NH_{3(aq)} \rightarrow 2\ [Cu(NH_3)_4]^{2+} + (CO_3)^{2-} + 2\ OH^-$$

$$2[Cu(NH_3)_4]^{2+} + CO_3^{2-} + 2\ OH^- + 2Sb_2O_3 \leftrightarrow 2Cu(SbO_2)_2 + CO_2\uparrow +\ H_2O + 8NH_3\uparrow$$

$$CuCO_3.Cu(OH)_2 + 8NH_{3(aq)} + 2Sb_2O_3 \leftrightarrow 2CuSb_2O_4 + CO_2\uparrow + H_2O + 8NH_3\ \uparrow$$

Experimental

Materials

Twinkling Star technical grade grade antimony trioxide (CAS-No. [1309-64-4]) powder was supplied by China MinMetals. Copper carbonate hydroxide (basic copper carbonate, CAS-No. [12069-69-1]) and ammonia solution 25 % (CAS-No. [1336-21-6]) were obtained from Merck.

Synthesis procedure

The NH_3 solution was placed in a round bottom flask fitted with magnetic stirrer and a reflux condenser. Electronic pH and temperature probes were used to measure the pH and the temperature in the flask, respectively. The ammonia was present in excess (1.1 or 1.2 times the stoichiometric quantity). The $CuCO_3.Cu(OH)_2$ powder was added in small portions to the NH_4OH solution as the dissolution/reaction is exothermic. Following full dissolution, the Sb_2O_3 powder was added to the copper ammonia complex and the reaction mixture was heated while stirring vigorously.

In a typical example, 10 g of copper carbonate hydroxide was suspended in 28.25 g of ammonia solution (25 % aq.) and 282 g of distilled water in a three neck flask and stirred at 500 rpm. An amount of 26.35 g of antimony trioxide was added and the mixture was heated on an oil bath to reflux temperature controlled at either 65 or 70 °C. The stirrer speed was set at 700 rpm to ensure complete suspension of the solids. Cooling water was passed through the condenser to prevent ammonia escaping. After a predetermined time, e.g. 6 h reflux, the cooling water was shut down and the ammonia was allowed to evaporate. The crystals were recovered by filtration.

During the reaction, homogeneous aliquots were taken from the reaction flask at regular time intervals. The sample vials were immediately placed in an ice-bath to arrest the

reaction. The solids settled out rapidly and the supernatant liquid was decanted. UV-Vis absorption spectra were recorded on a Perkin Elmer Lamda 25 UV/Vis spectrometer using polystyrene cuvettes with a path length of 10 mm. The copper concentration was estimated from the absorbance at 620 nm.

The Beer-Lambert absorption constant was determined using a calibration curve that was generated from known aqueous solution concentrations. These calibration samples were prepared by reacting the copper hydroxide carbonate with ammonia solution (20 % stoichiometric excess) followed by dilution with distilled water to the required copper concentration in g/L. The absorption peak was located between 620 and 624 nm for all samples tested. Beer's law constant was determined as $\varepsilon L = A/c = 0.244$ L/g $Cu(NH_3)_4$ in solution.

Characterization

The product powder samples were coated five times with gold using a SEM Polaron E5200. SEM images were obtained using an ultrahigh resolution field emission SEM (HR FEGSEM Zeiss Ultra Plus 55) with an InLens detector at acceleration voltages of 20 kV to ensure maximum resolution of surface detail.

Powder diffraction data was recorded on a Bruker D8 Advance diffractometer with a 2.2 kW Cu long fine focus tube (CuKα, λ=1.54060) and LynxEye detector with 3.7º active area. Samples were scanned at generator settings of 40 kV and 40 mA. A sub-sample of the fine bright green powder was pressed into a shallow plastic sample holder against a rough filter paper in order to ensure random orientation. X-ray diffractograms were also recorded after heating the material in air for 2 hours at 1100°C.

Thermogravimetric analysis (TGA) was performed using the dynamic method on a Mettler Toledo A851 TGA/SDTA instrument. About 15 mg powder was placed in an open

150 µL alumina pan. Temperature was scanned from 25 to 1000 °C at a scan rate of 10 °C/min with air flowing at a rate of 50 mL/min.

Results and Discussion

Figure 1 shows the change in the concentration of the copper complex over time for two runs conducted with the ammonia level set at 10 % stoichiometric excess. There is an initial rapid drop in the concentration to less than half the initial value within the first half hour. Thereafter the concentration stabilizes. This indicates that equilibrium between the copper antimonite and the copper complex was reached. Figures 2 and Figure 3 show results for similar experiments except that the cooling water is shut down after various times, allowing the ammonia to distil off. A further drop in the copper complex concentration is observed indicating that the reaction with antimony trioxide is driven to completion. A corresponding drop in the solution pH from 12.5 to ca. 7.5 was also observed. In all cases the yield of solids exceeded 97 % of the theoretical amount.

Figure 4 shows a SEM photograph of the final product powder. The crystalline particles with a cuboid morphology range in size from 1 µm to about 4 µm. Figure 5 shows the XRD diffractograms for the neat product and a the sample that was obtained following heat treatment for 2 h at 1000°C in air. The XRD diffractogram of the calcined sample showed an exact match to that of the $CuSb_2O_6$ standard listed in the XRD data bases. The TG trace shown in Figure 5 showed a mass increase of 7.8 wt% when the product was heated to 1000°C. This confirms the nature of the product as $CuSb_2O_4$ because the observed mass increase is consistent with the expected 8.6 wt% mass increase for the reaction with oxygen shown in Scheme II.

Scheme II: $CuSb_2O_4 + O_2 \leftrightarrow CuSb_2O_6$

Detailed analysis of the crystal structure of $CuSb_2O_4$ will be reported in a separate communication.

Conclusions

Well-crystalized copper antimonite ($CuSb_2O_4$) powder was successfully produced by reacting antimony trioxide with the copper-ammonia complex. Good yields were obtained by refluxing in the presence of 20% stoichiometric excess of ammonia for at least one hour at 65 °C and then allowing the ammonia to distil off.

Acknowledgements

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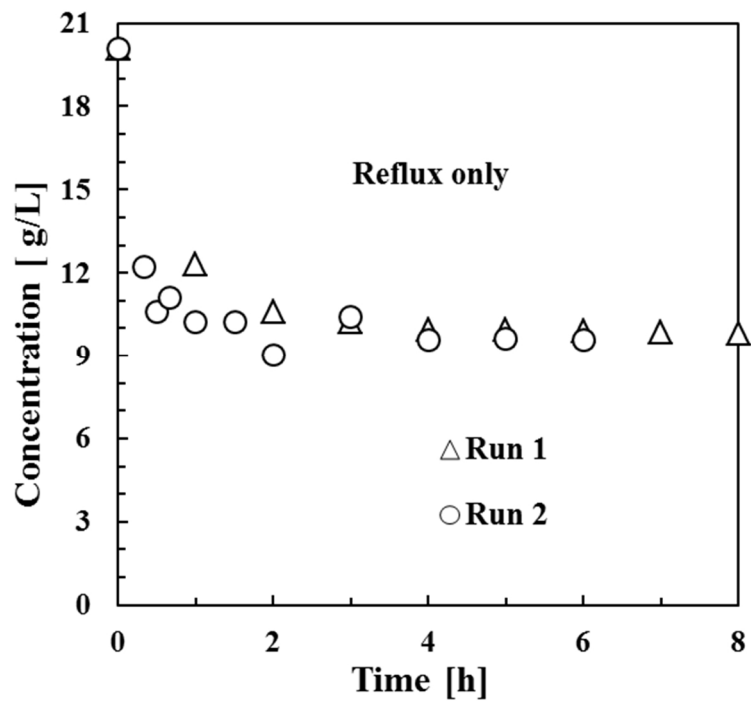
LIST OF FIGURES

Figure 1. Change in copper complex concentration with time when the reagents were refluxed at 65 °C. The ammonia excess was 10 %. The symbols ○ and △ represent data points obtained during two different experimental runs.

7

Figure 2. Change in copper complex concentration with time when the reagents were refluxed at 70 °C. The ammonia excess was 20 %. Reflux was stopped after 9 h by closing off the cooling water supply. Data points for two different experimental runs are shown. Open and solid symbols correspond to reflux and ammonia evaporation regimes respectively.
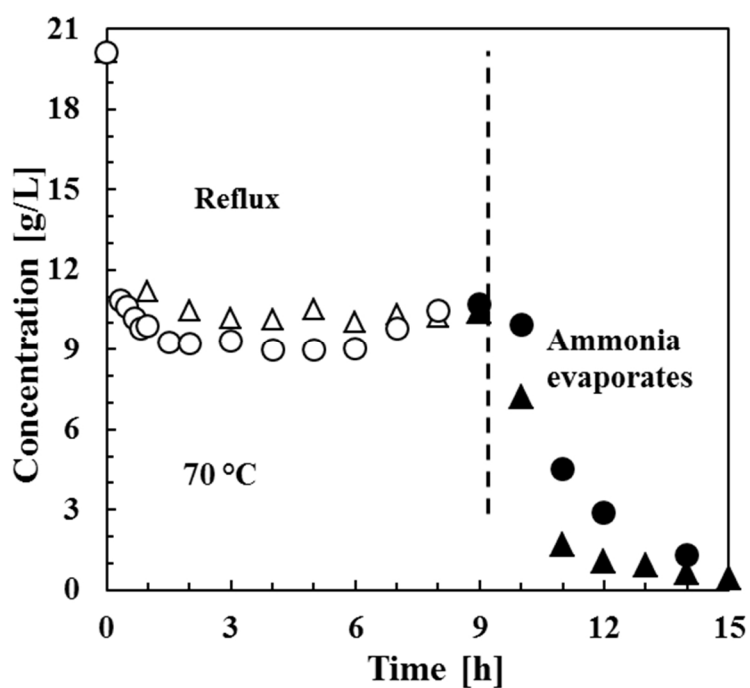
Figure 3. Change in copper complex concentration with time when the reagents were refluxed at 65 °C. The ammonia excess was 20 %. Reflux was stopped after 4.5 h or after 1 h by closing off the cooling water supply. Data points for two different experimental runs are shown. Open and solid symbols correspond to reflux and ammonia evaporation regimes respectively.

Figure 4. SEM micrograph of copper antimonite produced by the reflux method.

Figure 5. TGA trace for the synthesized $CuSb_2O_4$ heated at 10°C/min in air.

Figure 6. XRD diffractogram for the synthesized $CuSb_2O_4$ compared to a heat-treated sample calcined at 1100 °C.

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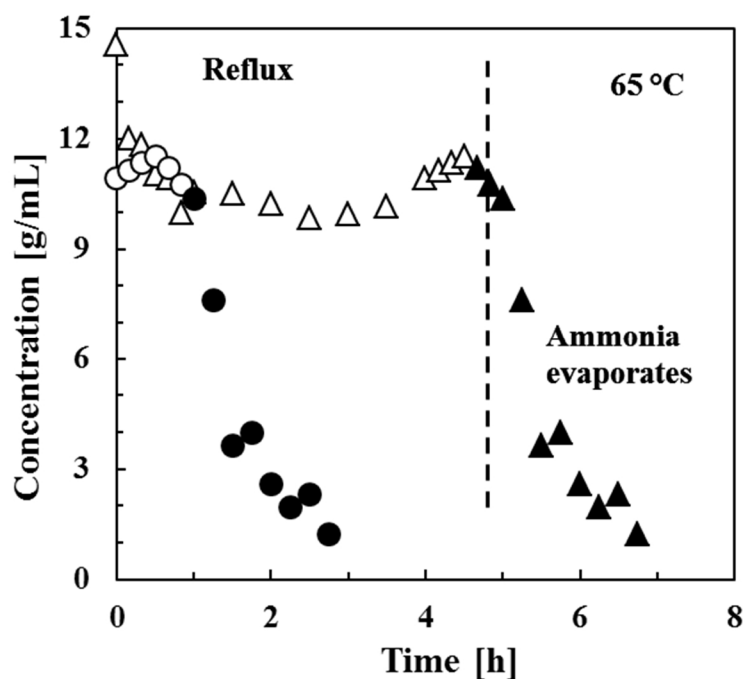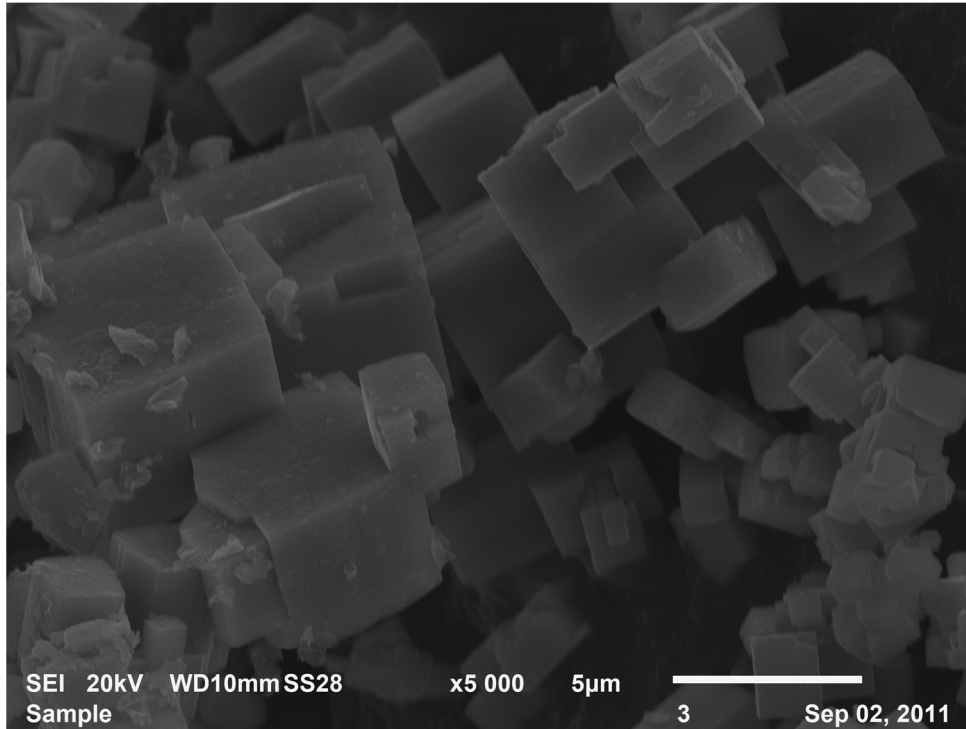
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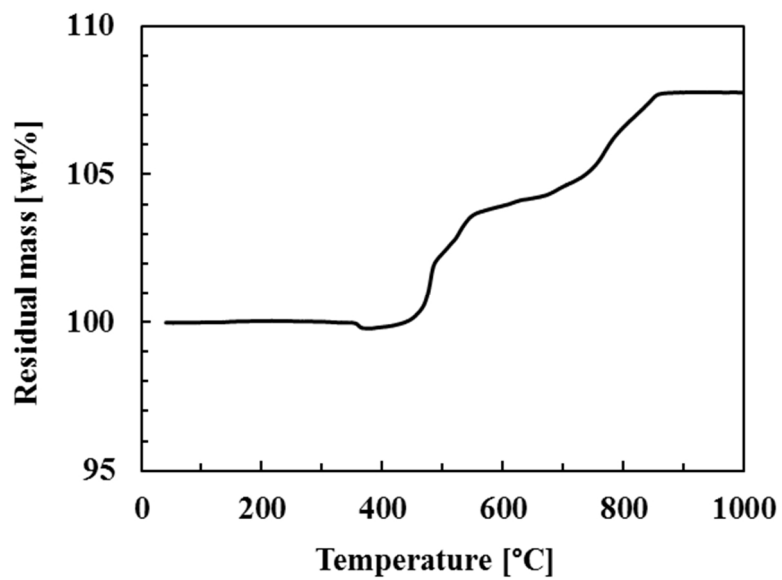
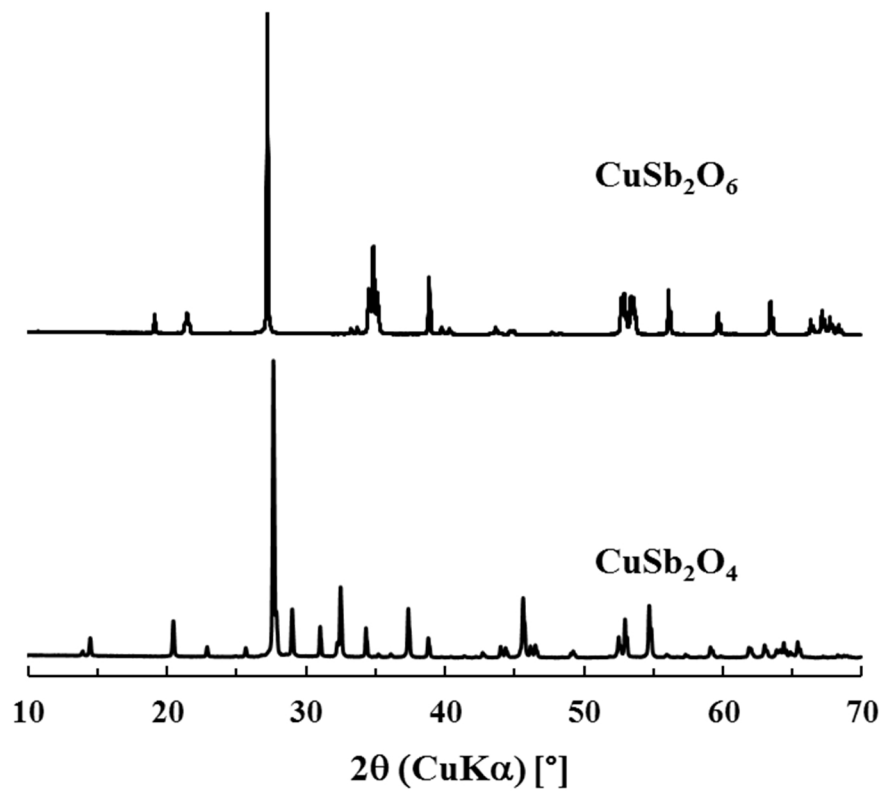**Figure 5.** TGA trace for the synthesized $CuSb_2O_4$ heated at 10°C/min in air.

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