OFFICE OF NAVAL RESEARCH

Contract #N00014-99-1-0538

R&T Code -
PR Number 01PR01106-00
Dr. Richard T. Carlin

Technical Report # 2

"A new method to prepare polycrystalline meta-thioboric acid, $(HBS_2)_3$"

by

Annamalai Karthikeyan, Chad A. Martindale and Steve W. Martin

Submitted for publication in

Inorganic Chemistry (Communications)

Department of Materials Science and Engineering
Iowa State University of Science and Technology
Ames, IA 50011, USA

September 25, 2001

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited

---

REPORT DOCUMENTATION PAGE

2.September 25, 2001

3. Interim Report

4. A new method to prepare polycrystalline meta-thioboric acid, $(HBS_2)_3$.

5. Contract #N00014-99-1-0538

6. Annamalai Karthikeyan, Chad A. Martindale and Steve W. Martin

7. Professor Steve W. Martin
Department of Materials Science and Engineering
Iowa State University of Science and Technology
Ames, IA 50011, USA

8. Technical Report # 2

9. Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

11. *Inorganic Chemistry (communications)*, submitted.

13. Abstract:

Thioacids (ex: thioboric acid) are important precursors in exploring new chalcogenide ceramic and glassy materials. We report here a new facile method to prepare crystalline meta-thioboric acid (c-$(HBS_2)_3$). c-$(HBS_2)_3$ was prepared by reacting H_2S with B_2S_3, in the vapor phase and the product was obtained as a vapor condensate. The technique is fairly simple and quick compared to the time consuming and wet routes of thiolysis of boron tribromide. The reaction takes place at much lower temperatures and in the vapor phase, thus achiveing higher purity.

14. Subject terms: thio-acids, thioboric acids, new preparation route, IR, Raman.

15. No. of pages:

16. Price code:

17. Unclassified:

A new method to prepare polycrystalline meta-thioboric acid, $(HBS_2)_3$

Annamalai Karthikeyan, Chad A. Martindale and Steve W. Martin*

Department of Materials Science and Engineering, Iowa State University of Science and Technology, Ames, IA 50011, USA

RECEIVED DATE (will be automatically inserted after manuscript is accepted).

The sulfur analogue of boric acid, $(HBS_2)_3$, is an important precursor to many thioborate glasses and polycrystals. However, only a few reports are available on the preparation routes of thioboric acids and their characterization is not well documented. Commonly, thioboric acid was obtained as an initial product leading to the preparation of B_2S_3. Moissan[1], and Stock and Poppenberg[2] reported the earliest preparation of thioboric acid. The preferred routes of preparation of thioboric acid are (i) thiolysis of boron tribromide with hydrogen sulfide[2,3] , and (ii) the reaction of amorphous boron with hydrogen sulfide[1,4,5] to obtain $(HBS_2)_3$. There are also other limited reports of the preparation of other thioacids, such as the sulfonization of bromic iodide and subsequent reaction with H_2S to obtain $H_2B_2S_5$[6]. The purity of the samples ($(HBS_2)_3$ and B_2S_3) obtained by all these procedures were poor and also no satisfactory purification process has been developed. In addition, the relative amounts of the trimer $(HBS_2)_3$ and the dimer $(HBS_2)_2$ present in the samples and their structures have not been fully determined. We report here a new facile method to prepare high-purity crystalline meta-thioboric acid $(HBS_2)_3$ and its characterization.

Optimized schemes for the preparation of high purity vitreous B_2S_3 (v-B_2S_3) directly from the elements has been reported from this laboratory[7]. This reaction was carried out at 850° C in a carborized and sealed silica tube and yields v-B_2S_3 with very little oxide and H_2S contamination. High-purity meta-thioboric acid was prepared using this v-B_2S_3 as described below. A known quantity of finely ground v-B_2S_3 was placed in a vitreous carbon crucible which was then placed in a silica reaction tube as shown in Fig.(1). A narrow alumina lance was inserted deep into the glassy powder. The silica reaction tube, crucible, and lance were well dried before assembly and the experiment was set up inside a glove-box filled with pure He (< 5 ppm O_2 & H_2O). The reaction setup was first flushed with N_2 and then filled with H_2S gas (99.5%). The reactor was then heated to ~ 350 °C. When the v-B_2S_3 in the carbon crucible was fully molten, a steady flow of H_2S, bubbling through the molten B_2S_3, was maintained at the rate of ~ 6 ml/min. The temperature of the reactor was then raised to 500 °C. The H_2S reacted with B_2S_3 and produced $(HBS_2)_3$ as a white vapor according to $3/2B_2S_3 + 3/2H_2S \rightarrow (HBS_2)_3$.

The white $(HBS_2)_3$ vapor condensed at the upper and cooler part of the reactor. Initially, a white foggy coating was seen and later, as the reaction proceeded for longer times, a thick band of white vapor condensate was obtained in this cooler part of the reactor. Other parts of the reactor above this band had only a very thin coating of the vapor and some needle-type crystal growth. The unreacted H_2S gas leaving the reactor was bubbled through a solution of NH_4OH and H_2O_2. This oxidized most of the H_2S to form sulfuric acid which was then neutralized by the ammonium hydroxide. The reaction was carried out for ~ 4-5 hours. The H_2S flow was then stopped and the reactor was flushed with N_2 and cooled.

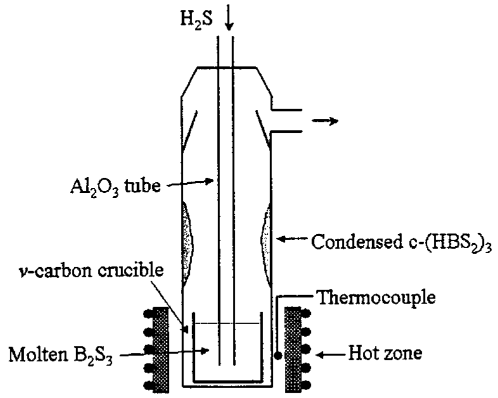

Figure 1. Reactor used in the preparation of $(HBS_2)_3$. The setup was used in a He filled glove box.

Samples from different parts of the tube were collected and examined. The reaction yielded ~ 1 gram/hour at the main condensing zone for a H_2S flow rate of ~ 6 ml/min. The condensates in the other parts of the tube were only about 0.3 grams. Faster reaction rates were easily obtained by increasing the flow of H_2S and the reaction temperature, but it was difficult to control the condensation zones. Further, increasing the temperature caused silica contamination in the product.

The powder diffraction pattern of the sample collected from the main condensing zone was recorded using a Scintag x-ray diffractometer. The sample powder was held in a plastic sample holder and sealed with Teflon tape. The diffraction pattern of the sample was obtained after eliminating the diffraction peaks of Teflon. The peak positions of the sample obtained in this study matched well with reported diffraction pattern of c-$(HBS_2)_3$ in the monoclinic structure[8,9].

Elemental analysis of the sample was carried out for sulfur and hydrogen using a PE-2400 Series II CHN/S elemental analyzer. The analysis showed 82% sulfur and 1% hydrogen (±0.3%), respectively. This is close the theoretical weight percent of 84.44% and 1.33%, respectively, for sulfur and hydrogen in $(HBS_2)_3$.

The IR spectrum (obtained using a Bio-Rad FTS-40 FT-IR spectrometer, on a pressed KBr pellet) and the Raman spectrum (obtained using a Bruker RFS 100/S FT-Raman spectrometer; Nd-YAG 1064 cm^{-1} laser line; Ge-detector in a

---

[1] Moissan, H. *C. R. Hebd. Seanes Acad. Sci.* **1892**, 115, 203.
[2] Stock, A.; Poppenberg, D. *Chem. Ber.* **1901**, 34, 399.
[3] Wiberg, E.; Sturm, W. *Z. Naturforsh* **1953**, 8b, 530.
[4] Greene, F.T.; Gills, P.W. *J. Am. Chem. Soc.* **1962**, 84, 3598.
[5] Greene, F.T.; Gills, P.W. *J. Am. Chem. Soc.* **1964**, 86 3964.
[6] Schmidt. M.; Siebert, W. *Chem. Ber.* **1969**,102, 2752.
[7] Martin, S.W.; Bloyer, D.R. *J. Am. Ceram. Soc.* **1990**, 73(11), 3481.
[8] Thomas, D.; Tridot, G. *C R. Hebd. Sean. Acad. Sci.*, **1964**, 259, 3559.
[9] Gates, A.S.; Edwards, J.G. *Inorganic Chemistry* **1977**, 16(9) 2248.

180° backscattering geometry) of the samples were recorded and are shown in Fig.(2). The H-S bonding in the compound is shown by the strong IR and Raman absorption at ~ 2535 cm^{-1}. The IR spectrum shows two broad absorption bands, between 750-950 cm^{-1} (with absorption peaks at 793, 870, 939 cm^{-1}) and 950-1050 cm^{-1} (with absorption peaks at 1020, 1046 cm^{-1}). These peak positions match well with the previously reported IR absorption peak positions of thioboric acid, $(HBS_2)_3$[9]. The IR spectrum of pure v-B_2S_3 exhibits (not shown) two dominant bands at ~760 cm^{-1} and ~1000 cm^{-1} and are due to $BS_{3/2}$ planar trigonal modes and 6-membered $B_3S_3S_{3/2}$ rings formed by linking trigonal boron units, respectively. In $BS_{3/2}$, 3 denotes the coordination and 2 denote its connectivity. Except for the small shift in the peak position and splitting, the two bands observed in $(HBS_2)_3$ correspond well with those of pure v-B_2S_3. The increased sharpness and the shift in the peaks observed in thioboric acid are due to the crystalline nature of the sample.

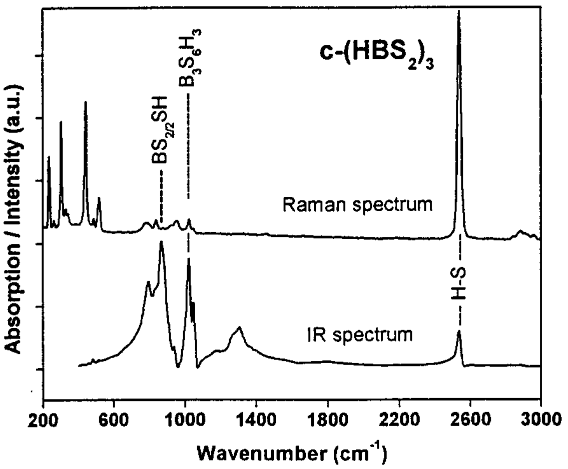

Figure 2. IR and Raman spectra of the c-$(HBS_3)_3$.

In a thioborate network, the addition of alkali sulfides leads to the change in coordination of the boron (from trigonal to tetragonal). It is interesting to note that in thioboric acid no such conversion is observed. The signature of the tetrahedral units appears at ~ 650 cm^{-1} in the IR spectra[10] and this band is absent in the IR spectra of $(HBS_2)_3$. The addition of H_2S to B_2S_3 only creates terminal proton (H-S-$B_{2/2}$) structures. In meta-thiboric acid, every $BS_{3/2}$ unit is converted into a $BS_{2/2}S$ unit. The alkali meta-thioborate phases have been prepared and characterized[10]. The Na, K, and Rb meta-thioborate phases are isostructural with meta-thioboric acid and are comprised of the planar six-membered ring $M_3B_3S_6$ units. Cs meta-thiborate also forms a ring unit from trigonal $BS_{3/2}$ units, but these rings are four-membered $Cs_2B_2S_4$ structures. Finally, Li meta-thioborate forms a very different structure based on $BS_{4/2}$ units that forms an adomantane-like structure of stoichiometry $Li_{10}(B_{10}S_{18})S_2$[10].

Some of the IR peaks are also present in the Raman spectrum, but in addition the Raman spectrum show additional peaks at lower wavelengths, 236, 303, 440, and 515 cm^{-1}. The peak observed at 440 cm^{-1} is attributed to the symmetric stretching of sulfur atoms in 6-membered (trimer units) – $(HBS_2)_3$. Evidence for the formation of 4-membered (dimer units) – $(HBS_2)_2$ rings is not seen in the Raman and IR spectra. Therefore, meta-thioboric acid is predominantly composed of 6-membered rings (trimers). The weak IR band observed at ~ 1180 cm^{-1} and a medium strength IR band observed at ~ 1310 cm^{-1} are due to oxide contamination in the sample. This oxide contamination comes from the oxides present in the v-B_2S_3 starting material and is estimated to be less than a few percent, much lower than that compared to the samples prepared by other procedures[7].

The preparation method described here has the following salient advantages over the earlier procedures. The technique is simple and quick compared to the time consuming wet route of thiolysis of boron trobromide with H_2S. The reaction takes place in the gaseous phase and the high purity of the sample is easily achieved. Although the new procedure looks like a reverse route (to some extent) to the earlier preparation method (of reaction of amorphous boron with H_2S at $\geq$ 700 °C), the technique has the foremost advantage of lower reaction temperatures (350 – 500 °C). Thus it is possible to carry out this reaction in silica tubes without contamination.

We have attempted to prepared vitreous $(HBS_2)_3$ by melting thioboric acid in a sealed silica tube and quenching it in water and liquid nitrogen, yet no glassy phase could be obtained. This is due to the terminated ring structure of $(HBS_2)_3$ (molecular solid) as explained above. The protons terminate the connectivity of these rings and hence the polymeric network essential for the formation glassy phase is not met. The other alkali meta-thioborate phases also are not strongly glass forming. The sodium metathioborate phase cannot be quenched to a glass at all and the other alkali meta-thioborate phases must be severely quenched to yield glasses. The quenched $(HBS_2)_3$ samples were bulk and crystalline with a density of 1.68 g/cm^3, which is about 3% less than that of v-B_2S_3. Presently, we are attempting to prepare other protonated phases using the $(HBS_2)_3$ acids, with suitable additions and modifications.

Acknowledgement. This work was funded by the Office of Naval Research, award number N00014-99-1-0538.

Supporting Information Available. A table listing the Infrared and Raman peak positions of c-$(HBS_2)_3$, prepared by earlier and present methods.

---

[10] Martin, S.W.; Cho, J. *J. Non-Crystalline Solids* **2001** (Submitted).

Table 1. Infrared (cm^{-1}) and Raman spectra (cm^{-1}) of the c-$(HBS_2)_3$ prepared by the current procedure and previous procedure (vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh - shoulder).

Infrared[1a]	Infrared[1b]	Infrared[2]	Raman[2]
2552 vw	2553 w	2535 m	2535 vs
1050 sh	1055 sh		
1041 m	1046 m	1046 m	1046 w
1031 sh	1034 sh		
1018 s	1022 s	1020 s	1020 w
938 w	942 w	939 w	956 w
915 sh	923 sh		920 w
895 w	898 w		
879 m	884 s	884 sh	
863 vs	867 vs	870 vs	839 w
787 m	793 m	793 m	793 w
			515m
			440 s
			303 s
257 w	256 vw		236 m

[1] Gates, A. S.; Edwards, J. G. *Inorganic Chemistry* 1977, 16(9) 2248 (a - prepared by reacting B and H_2S; b – prepared by thiolysis of BBr_3 with H_2S).

[2] Present work (the simpler IR spectra and stronger H-S peak (at 2535 cm^{-1}), compared to the earlier methods, signifies the higher phase homogeneity and purity of the sample).

Synopsis Thioacids (ex: thioboric acid) are important precursors in exploring new chalcogenide ceramic and glassy materials. We report here a new facile method to prepare crystalline meta-thioboric acid (c-$(HBS_2)_3$). c-$(HBS_2)_3$ was prepared by reacting H_2S with B_2S_3, in the vapor phase and the product was obtained as a vapor condensate. The technique is fairly simple and quick compared to the time consuming and wet routes of thiolysis of boron tribromide. The reaction takes place at much lower temperatures and in the vapor phase, thus achiveing higher purity.