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BROWN UNIV PROVIDENCE RI DEPT OF CHEMISTRY  
PREPARATION OF O17-LABELLED GLASSES AND GLASS PRECURSORS.(U)  
DEC 79 J A ABYS, D M BARNES, S FELLER  
TR-79-03

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N00014-75-C-0883

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TECHNICAL REPORT NO. TR-79-03

DDC FILE COPY ADA 080811

Preparation of  $O^{17}$ -Labelled Glasses and Glass Precursors

by

J. A. Abys, D. M. Barnes, S. Feller, G. Rouse and William M. Risen, Jr.

Prepared for Publication

in the

Materials Science Bulletin

December 10, 1979

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December 10, 1979

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER (14) TR-79-03	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) (6) Preparation of O <sup>17</sup> -Labelled Glasses and Glass Precursors		5. TYPE OF REPORT & PERIOD COVERED (9) Technical Repts	
7. AUTHOR(s) (10) J. A. Abys, D. M. Barnes, S. Feller, G. Rouse, William M. Risen, Jr		8. CONTRACT OR GRANT NUMBER(s) (15) N00014-75-C-0883 N00014-75-C-0883 N00014-75-C-0883	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Brown University Providence, Rhode Island 02912		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (11) 10 Dec 79	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research United States Navy		12. REPORT DATE December 10, 1979	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 152		13. NUMBER OF PAGES 14	
		15. SECURITY CLASS. (of this report)	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Distribution Unlimited; Approved for Public Release			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) isotopically labelled glass, Oxygen-17, synthesis, ionic oxide glasses, oxide glasses			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Novel methods for the preparation of O-17 labelled ionic oxide glasses which are label conservative and yield glasses at the same enrichment level as the starting materials, were designed to provide materials for the investigation of the O-17 NMR and the vibrational spectra. These methods are detailed for both oxygen-labelled network formers, B <sub>2</sub> O <sub>3</sub> and SiO <sub>2</sub> , and network modifiers, Li <sub>2</sub> O and LiOH. Routes are suggested for related network formers and modifiers.			

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## PREPARATION OF $O^{17}$ -LABELLED GLASSES AND GLASS PRECURSERS

J. A. Abys, D. M. Barnes, S. Feller, G. B. Rouse, and W. M. Risen, Jr.  
 Dept of Chemistry, Brown University, Providence, Rhode Island 02912 U.S.A.

### ABSTRACT

Novel methods for the preparation of  $O^{17}$  labelled ionic oxide glasses which are label conservative and yield glasses at the same enrichment level as the starting materials, were designed to provide materials for the investigation of the  $O^{17}$  NMR and the vibrational spectra.

### Introduction

Nuclear magnetic resonance and vibrational studies have contributed much to understanding the structure and bonding of inorganic glasses and other complex oxygen-containing solids. For example, the short-range order and internal motion in oxide glasses has been probed sensitively by NMR studies employing the  $B^{10}$ ,  $B^{11}$ ,  $Li^7$ ,  $Na^{23}$  and  $Tl^{205}$ , and other nuclei (1-4). But, until recently the striking omission from the list of nuclei whose resonances have been used to probe glass structures has been oxygen-17 (5).

The only isotope of oxygen with a magnetic moment is  $O^{17}$ , and it is not useful in conventional NMR at its natural abundance level of 0.03%. Enriched water has become available, although at high cost, with enrichments of up to 50% in  $O^{17}$  and 40-50% in  $O^{18}$ . This makes it feasible to perform  $O^{17}$ -NMR studies and vibrational studies, with observable  $O^{17}$  and  $O^{18}$  isotopic shifts, on highly enriched materials. Significant quantities of material are required for the NMR studies of such solids, and pure materials (both chemically pure and with  $O^{17}/O^{18}$  labels undiluted with  $O^{16}$  from natural abundance sources) are required for both types of spectroscopy. Therefore, both cost and the need for purity demand synthetic routes by which the labelled water is incorporated completely into products without scrambling or is recovered. A number of such routes have been investigated and are discussed in this paper.

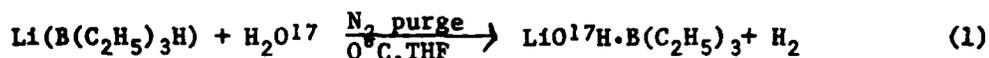
We report syntheses of inorganic solids that have been designed to yield pure products, having the same  $O^{17}$  enrichment level (6) as the labelled water used as starting materials, that provide the starting materials for isotopically labelled glasses. In addition, the routes are designed to have all of the  $O^{17}$  label either incorporated in the glasses or recovered in enriched water. The routes satisfy the design requirements, such as lack of scrambling and recovery or incorporation of water. The details of the syntheses of  $LiO^{17}H$ ,  $Li_2O^{17}$ ,  $B(O^{17}H)_3$ ,  $B_2O_3^{17}$  and  $SiO_2^{17}$ , which are also the starting materials for the  $Li_2O \cdot xB_2O_3$  and  $Li_2O \cdot xSiO_2$  glass systems are reported here (6). Synthetic routes for related materials are suggested and discussed.

### Glass Network Modifiers

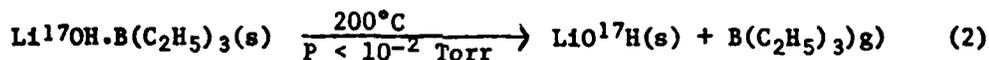
#### Synthesis of LiO<sup>17</sup>H and Li<sub>2</sub>O<sup>17</sup>

The standard synthetic routes (7) for preparing LiOH and Li<sub>2</sub>O involve the dehydration of LiOH·H<sub>2</sub>O, which can be obtained in a number of ways. These fall into several categories. One involves reaction of Li and H<sub>2</sub>O directly, but it is difficult to carry out so as to give pure products, i.e. free of carbonates and other oxides. Another involves reaction of Li<sup>+</sup> in solution with other hydroxides. The latter has some of the same problems as the direct reaction, and would present problems of label-scrambling and dilution due to rapid H<sub>2</sub>O/OH interchange. In the end, using it would merely move the synthesis problem back one step to the preparation of the hydroxide with which the Li<sup>+</sup> was to be reacted.

The approach employed here involves the hydrolysis of an organolithium compound, Li(B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H). This compound is commercially (8) available and is hydrolyzed in tetrahydrofuran (THF) at 0°C under N<sub>2</sub> according to the reaction:

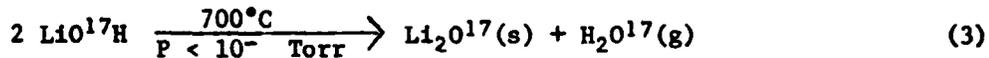


The triethylborane adduct is left in solution after the H<sub>2</sub> is swept away by the N<sub>2</sub> purge gas. Upon removal of the solvent the solid adduct is decomposed by heating under vacuum to yield pure LiO<sup>17</sup>H:



This product was obtained in greater than 99% yield and was shown by X-ray diffraction to be pure.

Thermal decomposition of LiO<sup>17</sup>H yields pure labelled Li<sub>2</sub>O<sup>17</sup> (6) with quantitative recovery of O<sup>17</sup> labelled water (by trapping on a vacuum line), according to the reaction:



The detailed procedures for these syntheses are given in the Experimental Section.

#### Related Network-Modifier Metal Oxides

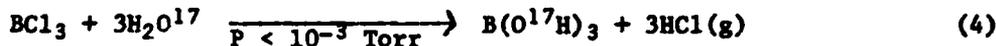
For O<sup>17</sup>-NMR studies of a range of ionic oxide glasses it is important to have alkali metal and alkaline earth metal oxides which are enriched to the level of the enriched water starting material. Analogous approaches to the one employed for LiO<sup>17</sup>H and Li<sub>2</sub>O<sup>17</sup> should be considered. Thus, for KO<sup>17</sup>H the commercially available compound K(sec-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>BH (7) may be hydrolyzed. In designing preparations of sodium, rubidium and cesium hydroxides in this manner, metal trialkylhydroborane starting materials which can be synthesized as starting material (7), should be considered.

A more suitable approach to obtaining the calcium, magnesium, strontium and barium hydroxides is through the careful hydrolysis of the hydrides, for example, CaH<sub>2</sub>. In the case of Mg(O<sup>17</sup>H)<sub>2</sub>, careful hydrolysis of Mg<sub>3</sub>N<sub>2</sub>, which yields NH<sub>3</sub> as a byproduct, should be examined.

If the peroxides of these metals are required for glass preparations, and their syntheses involve the use of H<sub>2</sub>O<sub>2</sub>, the enrichment level can be maintained by the use of double-labelled H<sub>2</sub>O<sub>2</sub> (9).

Glass Network FormersSynthesis of B<sub>2</sub>O<sub>3</sub><sup>17</sup>

A synthesis of B<sub>2</sub>O<sub>3</sub><sup>17</sup> which meets the requirements set forth above is based on the hydrolysis of BCl<sub>3</sub>, according to the reaction:



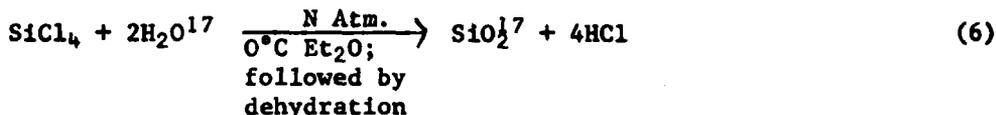
The product hydroxide is freed of HCl in vacuo, and is dehydrated, with the unused labelled water being trapped, according to the reaction:



This procedure leads to pure B<sub>2</sub>O<sub>3</sub><sup>17</sup>, as determined by X-ray crystallography, in greater than 95% overall yield. It is detailed in the Experimental Section.

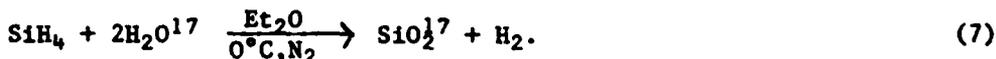
Synthesis of SiO<sub>2</sub><sup>17</sup>

The hydrolysis of SiCl<sub>4</sub> proceeds smoothly in diethyl ether (Et<sub>2</sub>O) without oxygen scrambling according to the reaction:



and removal of HCl, Et<sub>2</sub>O, and SiCl<sub>4</sub> under reduced pressure affords SiO<sub>2</sub><sup>17</sup> in high purity (6) and greater than 95% yield. Details are in the Experimental Section.

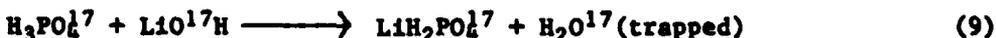
It is to be expected that a synthesis of SiO<sub>2</sub><sup>17</sup> which meets the requirements could be designed around the hydrolysis of silane, SiH<sub>4</sub>:



Although this proceeds under a variety of conditions, it proceeds smoothly in bulk only in the presence of alkali, so this approach was rejected.

Related Network-Former Oxides

In addition to these materials, which form the basis for borate, silicate, and related glasses, precursors for phosphate, aluminate, arsenate and other glasses are of interest. Since metaphosphate glasses are of importance, the design of the synthesis of an O<sup>17</sup>-labelled ionic metaphosphate, (LiPO<sub>3</sub><sup>17</sup>)<sub>n</sub>(gl) or (Li<sub>2</sub>O<sup>17</sup>·P<sub>2</sub>O<sub>5</sub><sup>17</sup>)(gl), may be considered as an example. Hydrolysis of phosphorus pentachloride, PCl<sub>5</sub>, yields phosphoric acid, which can be reacted with fully labelled LiOH to form LiH<sub>2</sub>PO<sub>4</sub><sup>17</sup> and that can be dehydrated to yield the glass. Thus, the synthesis can be approached using the following type of reaction sequence:

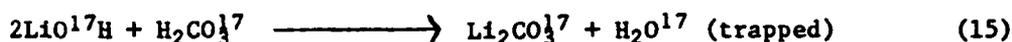


Analogous hydrolysis reactions with the hydrides, halides and organo-

element compounds of Al, As, Ge, and other elements resulting in network forming oxides can be employed in designing  $O^{17}$ -label-conservative, non-scrambling syntheses. In addition, certain carbides should be considered, such as  $Al_4C_3$ , which is hydrolyzed according to the reaction:



Frequently, though, the most convenient route to the ultimate glassy product involves reactions in which  $CO_2$ , rather than  $H_2O$ , is evolved. If labelled  $CO_2$  is not available, in order to construct an overall label-conservative, non-scrambling (with  $O^{16}$ ) synthesis it probably is simplest to begin with the electrolysis of  $H_2O^{17}$  to yield  $O_2^{17}$  with which  $C(s)$  is combusted in a closed system. Reaction of this  $CO_2^{17}$  with  $H_2O^{17}$ , forming  $H_2CO_3^{17}$  in equilibrium, leads to the carbonates required when reacted with, for example,  $LiO_2^{17}H$ . This approach avoids scrambling of the  $O^{17}$ -label with  $O^{16}$  from natural abundance compounds, but the final glass product syntheses proceed with the evolution of  $CO_2^{17}$  rather than  $H_2O^{17}$ . Although it is possible to convert the  $O^{17}$  in the  $CO_2^{17}$  formed back into  $H_2O^{17}$ , and although the  $H_2O^{17}$  starting material is expensive, it may be best simply to trap the  $CO_2^{17}$  and use it with  $H_2O^{17}$  to generate  $H_2CO_3^{17}$  for further reactions in a sequence of batches. The net  $CO_2^{17}$  loss in preparing any quantity of product then becomes a function of the number of batches made in synthesizing the desired amount of product. This is illustrated by the  $Li_2O \cdot 2SiO_2$  sequence:



The  $CO_2^{17}$  trapped in (16) and the  $H_2O^{17}$  trapped in (15) are to be recycled into reaction (14).

In certain of the silicate glass syntheses with carbonates, hydrous silica,  $SiO_2^{17} \cdot nH_2O^{17}$ , will be the desired reactant with the labelled carbonate. It can be obtained by the careful hydrolysis of  $Si_2H_6$ .

### Experimental

#### Synthesis of $LiO^{17}H$

The solvent for the hydrolysis reaction was THF, which was distilled twice under  $N_2$ , first after refluxing it over  $LiAlH_4$ , and second after preparing sodium benzophenone ketyl (Na BPK) in it (10). It was distilled from the Na BPK solution. The lithium-containing starting material,  $Li(B(C_2H_5)_3H)$ , (also known as L-selectride) was obtained in solution from the Aldrich Chemical Company (Milwaukee, Wisconsin), and the isotopically labelled water,  $H_2O^*$ , (52.79%  $H_2O^{17}$ , 41.79%  $H_2O^{17}$ , 5.42%  $H_2O^{16}$ ) was obtained from Prochem Company-U.S.A., (Summit, N.J.).

The first reaction, (1), releases  $H_2$  and should be carried out only as described. The apparatus shown in Fig. 1 consisted of glassware that was oven dried at  $120^\circ C$  for 24 hrs, assembled, and cooled in a stream of ultra-pure  $N_2$  (or pure Ar). While cooling with the  $N_2$  from tank 1 flowing slowly,

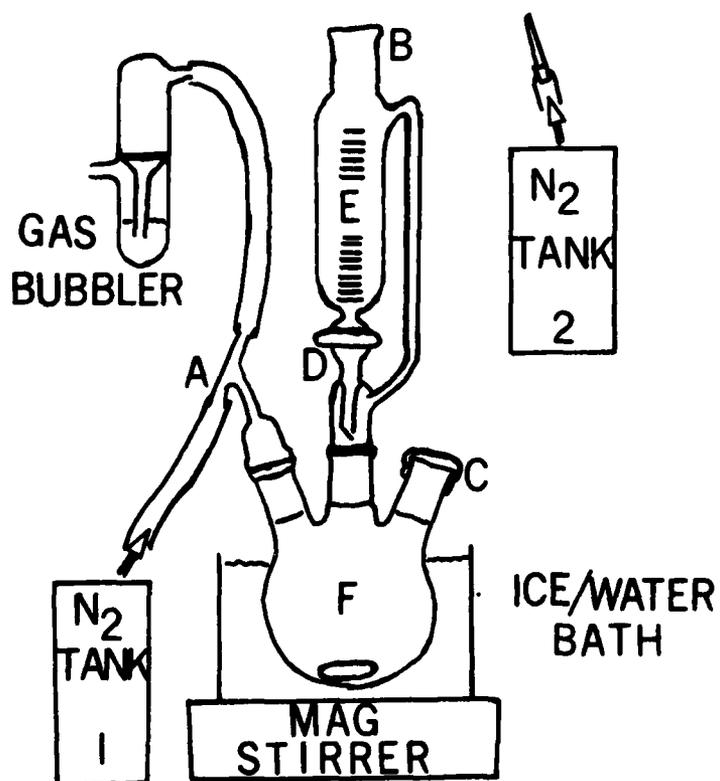


Figure 1

Experimental setup for the L-selectride hydrolysis

needle 2 was inserted through the rubber septum, B, and the system was flushed with the  $N_2$  gas for 1 hr with stopcock D open and for 0.5 hr with D closed. Then, needle 2 was removed and the  $N_2$  from tank 1 was allowed to flow at a higher rate, monitored by a mineral oil bubbler. After stopcock D was closed, 250 ml of freshly distilled THF was added to the 500 ml flask through septum C, and 155 ml (0.155 moles) of 1M L-selectride was transferred from the reagent bottle (fitted with a septum) under a slight  $N_2$  pressure to funnel E through septum B through a double-ended 25 cm syringe needle. The L-selectride was then allowed to flow into the 500 ml flask, F. An ice-water-salt bath (at ca.  $-5^\circ C$ ) was placed around flask F and the solution in F was stirred vigorously for 1 hr.

The stoichiometric amount of the  $H_2O^*$  was then placed in a constant addition, gas-tight syringe, and the needle was inserted through septum C. The  $H_2O^*$  was added to the L-selectride solution in 0.1 ml aliquots at the rate of 0.1 ml per 5 min. When the addition was complete, the solution was stirred for another 0.5 hr at ca.  $-5^\circ C$ , and then allowed to warm to room temperature. Stirring was continued for 1 hr. The resulting colorless solution was transferred under  $N_2$  through a double-ended syringe needle to a two neck recovery flask having a septum on the side port and a stopcock on the center port. The solvent was removed on a rotary evaporator (to which it was attached without exposure to the air) at  $1 \times 10^{-1}$  Torr. When the residue was solid the temperature was raised to  $100^\circ C$  for 1 hr. The resulting white powder product, mostly  $LiOH \cdot B(C_2H_5)_3$ , was ground to a fine powder in a  $N_2$ -filled dry box and placed in a round bottom flask, fitted with a vacuum stopcock. This was placed on a vacuum line where it was heated at  $250^\circ C$  and  $1 \times 10^{-3}$  Torr for 24 hr to remove the residual  $B(C_2H_5)_3$ . The  $B(C_2H_5)_3$  was trapped and recovered.

The product is  $LiO^*H$ , in 98% yield, and was checked for purity by X-ray diffraction. This confirmed its identity and indicated that it was purer than the highest grade commercial product.

#### Synthesis of $Li_2O^*$

The  $LiO^*H$  prepared as described above was placed in a silver-foil lined nickel boat, F, in a quartz tube, E, fitted as shown in Fig. 2. The heating tape, D, in Fig. 2, must not be closer to the neoprene stopper than 10 cm. With stopcock A closed, the vacuum pump was turned on, and A was opened slowly (to prevent the dry, powdered sample from flying around the tube while it is being evacuated). After evacuation of the tube, a liquid  $N_2$ -filled bath was placed around trap B. The heating coil temperature was raised to  $120^\circ C$ , and then the oven, G, temperature was raised to  $100^\circ C$  at the rate of  $2^\circ C/min$ , held at  $100^\circ C$  for 1 hr, raised to  $150^\circ C$  at the same rate, held at  $150^\circ C$  for 1 hr, raised to  $400^\circ C$  at that rate, held at  $400^\circ C$  for 1 hr, raised to  $450^\circ C$ , held at  $450^\circ C$  for 10 hrs, and finally raised at the same rate to  $700^\circ C$ , where it was held for 24 hrs. After the tube cooled to room temperature, dry  $N_2$  gas was admitted slowly and the sample was removed and stored in an  $N_2$ -filled desiccator.

#### Synthesis of $B_2O_3^*$

This synthesis was performed in the vacuum system shown in Fig. 3. It was evacuated to  $1 \times 10^{-3}$  Torr with stopcocks 1,2,4,5 and 6 open. Stopcock 3 was opened several times (in freeze-thaw degassing cycles) to remove air from the  $H_2O^*$ -containing tube and then closed. Stopcocks 1,4,5 and 6 were closed, liquid  $N_2$  was placed under flask B, and then stopcock 3 was opened and 3 ml (ca. 0.1621 moles) of  $H_2O^*$  (same as used in the  $LiO^*H$  preparation, above) was vacuum distilled into the reaction flask B. Stopcock 3 was

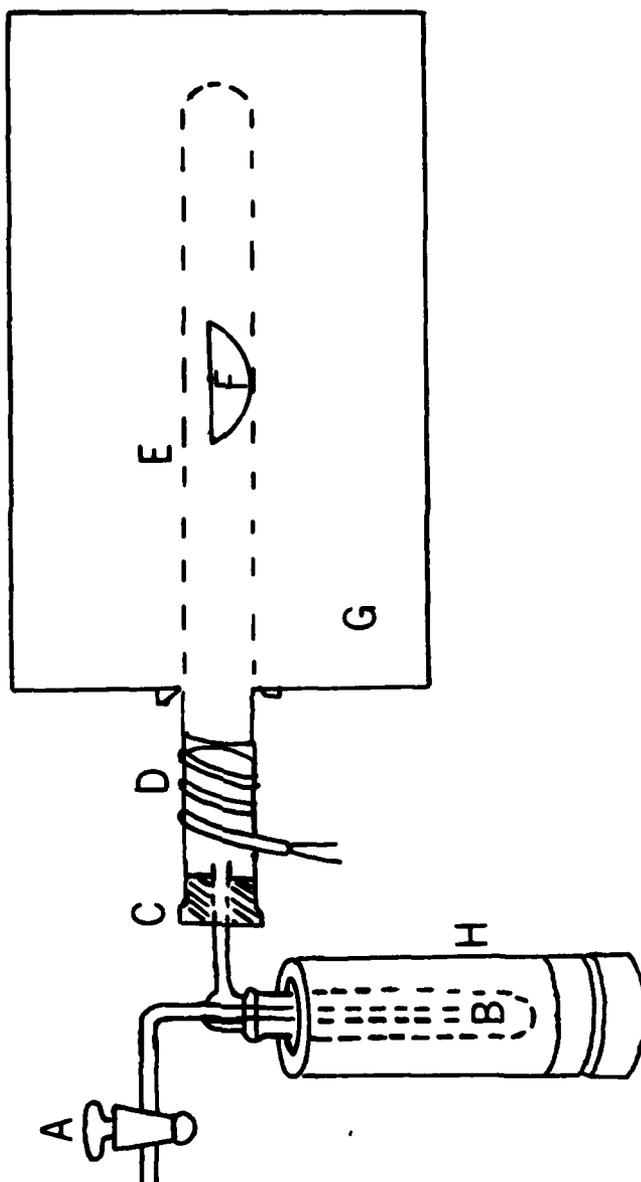


Figure 2

Experimental setup for the label-conservative  $\text{LiO}^*\text{H}/\text{Li}_2\text{O}^*$  conversion

then closed, 1 was opened, and then stopcock 1a was opened slowly to allow about 2g of  $\text{BCl}_3$  (about 30% of the 6.27g (0.0540 moles) of  $\text{BCl}_3$  required for a stoichiometric reaction) to enter the system. Then stopcocks 1 and 1a were closed. The safety of this step depends on the volume of D being great enough for all of the  $\text{HCl(g)}$  released in the reaction to be accommodated at a pressure of less than 760 Torr. Therefore, when the approximately 30% of the  $\text{BCl}_3(\text{g})$  was added, it actually was added so as to bring the pressure in the system (with 1,4, and 6 closed) to 240 Torr. This is the approximate pressure if the volume of the system is ca. 1.25l when 1,4, and 6 are closed and 0.0162 moles of  $\text{BCl}_3$  are added. With this portion of the system filled with  $\text{BCl}_3(\text{g})$  at 240 Torr, stopcocks 1,1a,2,3,4, and 6 closed, a liquid  $\text{N}_2$  bath was placed around flask B, stopcocks 2 and 4 were opened and the  $\text{BCl}$  was condensed into B. The liquid  $\text{N}_2$  was removed, the reactants in B were warmed gently, and the reaction proceeded smoothly with evolution of  $\text{HCl(g)}$  as the pressure rose to a steady level (it reaches 500-700 Torr, depending on the volume of B and its connections). Then stopcock 2 was closed, and the  $\text{HCl(g)}$  pumped into the trap T (cooled by liquid N). The entire procedure was repeated three times, with additional 30,30, and 10% portions of the  $\text{BCl}_3(\text{g})$ . The pressure needed for the final  $\text{BCl}_3$  addition was carefully calculated to assure that it did not exceed the amount needed stoichiometrically. Following the last reaction step, any tiny excess  $\text{BCl}_3(\text{g})$  remaining was pumped off, then with B at liquid  $\text{N}_2$  temperature and 4 closed, a small amount of  $\text{H}_2\text{O}^*$  was distilled from C into B to react with the small excess of  $\text{BCl}$  remaining in B. Then, with C closed, the remaining  $\text{HCl(g)}$  was pumped off, leaving primarily hydrated  $\text{B(O}^*\text{H)}_3$  in B.

Finally, C was replaced with a new tube C', stopcocks 1 and 2 closed and the system evacuated to  $1 \times 10^{-3}$  Torr. Then with 4 closed and 2 and 3 open, C' was cooled with liquid  $\text{N}_2$  and B was heated to  $310^\circ\text{C}$ . The hydrated  $\text{B(O}^*\text{H)}_3$  was converted to  $\text{B}_2\text{O}_3^*$  and the  $\text{H}_2\text{O}^*$  was recovered in C'. The yield of pure  $\text{B}_2\text{O}_3^*$  was 99%.

#### Synthesis of $\text{SiO}_2^*$

The synthesis of  $\text{SiO}_2^*$  by reaction (6) was carried out in a 250 ml two-neck flask (one neck fitted with a septum and the other with a gas-purge tee similar to that shown in Fig. 1.  $\text{SiCl}_4$  from PCR Research Chemicals (11.83g, 0.0696 moles) was transferred in a  $\text{N}_2$ -filled dry box to the flask containing 100 ml of diethyl ether, freshly distilled under  $\text{N}_2$ , and the slow  $\text{N}_2$  purge through the tee was begun. The flask was placed in an ice bath over a magnetic stirrer. A constant-portion addition syringe was filled with 2.7g (0.139 moles) of  $\text{H}_2\text{O}^*$  and fitted with a gold-plated needle (to prevent corrosion by  $\text{SiCl}_4$  vapors). The solution was stirred vigorously surrounded by the ice bath as the  $\text{H}_2\text{O}^*$  was added in 0.1 ml increments over a period of about 1 hr. After complete addition of the  $\text{H}_2\text{O}^*$ , the mixture was warmed to room temperature and stirred for an additional 2 hr. This was continued until wet litmus at the gas outlet no longer showed the presence of  $\text{HCl(g)}$ . Then, the reaction flask was attached to a rotary evaporator and most of the ether and residual  $\text{HCl}$  removed. Finally, the product was heated at  $200^\circ\text{C}$  on a vacuum line for 24 hr. The yield of pure, X-ray amorphous  $\text{SiO}_2^*$  was 97%.

#### Acknowledgments

This work was supported in part by the Office of Naval Research. The support of the Materials Science Program at Brown University, under a grant from the National Science Foundation is gratefully acknowledged. The authors are grateful to Professor P. J. Bray and Mr. A. Geissberger of the Physics Department for assistance.

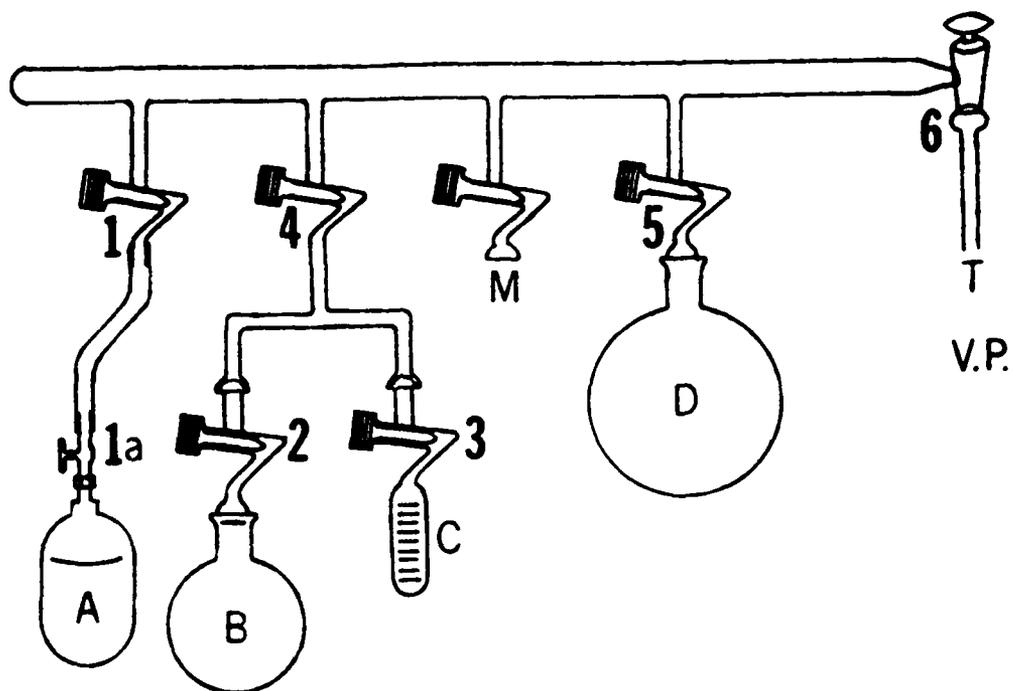


Figure 3 .

Experimental setup for the label-conservative synthesis of  $B_2O_3^*$ ; M = manometer, and T, V = trap and vacuum pumping system. The other labels are described in the text.

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