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ATOMIC WEAPONS RESEARCH ESTABLISHMENT

AWRE REPORT No. O - 53/61

A Preliminary Examination of Lithium Tetraborate

J. H. Sant

D. R. Gregory

A.W.R.E.

Aldermaston Berks

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November, 1961

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A Preliminary Examination of Lithium Tetraborate

J. H. Sant
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Summary

This report examines the literature and gives some experimental observations on the dehydration, composition, water absorption, density and melting point of lithium tetraborate supplied as the pentahydrate.

Recommended for issue by

546.34.273

D. Deverell, Superintendent

Approved by

P. A. White, Senior Superintendent

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1. INTRODUCTION

This report examines the published literature on lithium tetraborate and includes some experimental data which may assist in the characterisation of this material.

As more information becomes available it will be published in further reports.

2. LITERATURE SURVEY

2.1 Preparation

(a) Filsinger Synthesis [1]

Boil equivalents of boric acid and lithium carbonate until carbon dioxide is no longer evolved. On treatment with alcohol, a granular precipitate forms:-



(b) A repetition of Filsinger's Synthesis [1] by H. Gode [2] gave $\text{Li}_2\text{O} \cdot 0.236\text{B}_2\text{O}_3 \cdot 4.25\text{H}_2\text{O}$ rather than $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. However, in course of weeks, an aqueous solution of lithium carbonate formed a white fine crystalline precipitate which corresponded to $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

(c) The conditions for synthesising borates from aqueous solutions at room temperature were determined by H. Gode and A. Kežāns [3]. At constant pH the rate of crystallisation of borates increased sharply because the mutual transformation of polyborate ions, $\text{B}_4\text{O}_7^{--}$, $\text{B}_2\text{O}_4^{--}$, and $\text{B}_6\text{O}_{10}^{--}$, decreased.

2.2 Properties

H. Gode [2] reported that the fine white crystalline precipitate which corresponded to $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (see preparation (b), above) has a density of 1.88 g/cm^3 at 20°C and is soluble in water, 3.609 g in 100 ml . On heating, water is lost in one step between 200°C and 220°C ; the dehydrated compound melts at 850°C .

This is confirmed by the Ref. [4] that lithium tetraborate is a white crystalline powder, which loses water at 200°C. It is very soluble in water and insoluble in alcohol.

2.3 Phase Equilibria Studies

The reported results for various investigations which have been carried out [5 - 9] indicate a divergence of opinion, both as to the structure and true formula of the compound. Some sources quote $\text{Li}_2\text{B}_4\text{O}_7$, while others suggest $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$. The number of molecules of water of crystallisation attached to the hydrated compound also seems to be in doubt.

As early as 1904, Guertler [5] was the first to study borate anhydrides of lithium, cadmium, lead and manganese. Later (1926), C. Mazzetti and F. De Carli [6] undertook a detailed study of these compounds and reported results obtained by using Tammann's method. The technique used and the method of crystallising these glasses is described. The results of thermal analysis for the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ show characteristic points corresponding to the compounds $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$, $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$, $\text{Li}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, $\text{Li}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, the existence of the first two being certain.

More recently (1955), Rollet and Bouaziz [7] stated that:- hydrated lithium diborate, considered until now as an amorphous product, separates from aqueous solutions in the form of fine crystals which are slightly soluble in water. Study of the ternary system $\text{H}_2\text{O}-2\text{B}_2\text{O}_3\text{-Li}_2\text{O-LiCl}$ has shown that the formula of the hydrate is $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$.

Rollet and Bouaziz [8] also reported that a phase diagram had been constructed from data obtained by thermal analysis of heating curves and showed the existence of five previously unknown solids in addition to the already known monoborate, $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$, and diborate, $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$. The new solid phases include the orthoborate, $3\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$, the borate, $3\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, the triborate, $\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$, and two additional solid phases, of which one is probably a tetraborate and the composition of the other is unknown. All the new solid phases have incongruent melting points. The orthoborate forms fine needles and decomposes at 695°C which is below its melting point. The borate, $3\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, forms polyhedral crystals and decomposes at 685°C before melting. The triborate appears to decompose at 835°C - 845°C. An isothermal line at 790°C seems to show a tetra-

borate that would have a composition corresponding to $\text{Li}_2\text{O} \cdot 4\text{B}_2\text{O}_3$. Another isothermal line at 730°C seems to indicate a metastable equilibrium. The undetermined solid phase at this temperature and composition crystallises with an increase in volume.

Recently Sastry and Hummel have made a series of studies of lithium oxide systems. From their report No. V [9] the following is summarised:-

Quenching and differential - thermal - analysis methods were used to study the high - Li_2O portion of the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$. A complete phase diagram is presented. Compounds formed include $3\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, with an incongruent melting point at $700^\circ + 6^\circ\text{C}$, $3\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$, with an incongruent melting point at $715^\circ + 15^\circ\text{C}$, and $2\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$, which dissociates below $650^\circ + 15^\circ\text{C}$. The entire system is characterised by low fusion temperatures, with all liquidus temperatures below $917^\circ + 2^\circ\text{C}$, the congruent melting point of the compound $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$.

3. PRELIMINARY EXPERIMENTAL EVALUATION OF LITHIUM TETRABORATE

3.1 Dehydration

It was found that when a sample of lithium tetraborate supplied as the pentahydrate was exposed to the normal laboratory atmosphere for 48 h it suffered a weight loss approximating to 2 molecules of water. A sample was submitted for analysis by the Stanton thermo-balance [10] and it was found that further loss in weight occurred up to 400°C when a constant weight was obtained. This accounted for a further 3 molecules of water being lost. On heating the sample to 1400°C no further weight change occurred due to water loss, but at 1200°C a slight loss was noted due to sublimation of the material. A check determination starting with material as supplied, heated to 420°C to give a constant weight, lost in all approximately 4.6 molecules of water. A slight unaccountable loss in weight due to some efflorescence at room temperature would make up the water content to about 5 molecules per molecule of lithium tetraborate.

3.2 Composition

The above dehydration tests together with an analytical determination of lithium and boron content [10] confirmed that the material as supplied had an empirical formula of $\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$.

The determined lithium content was 5.72% and boron content 16.6%, compared with the theoretical values of 5.4% and 16.7% respectively. Analysis of the anhydrous material gave a lithium content of 8.1%, compared with a theoretical lithium content for $\text{Li}_2\text{B}_4\text{O}_7$ of 8.2%. The anhydrous material was therefore assumed to be in the correct stoichiometric proportions.

On heating lithium tetraborate to 900°C it fused to a water white liquid which on rapid cooling solidified to a clear glass. Very slow cooling from the fused state yielded a crystalline material which on visual examination under a Vickers microscope appeared to be a mixture of cubic and hexagonal crystals. Lithium tetraborate therefore seems to be isomorphous with sodium tetraborate.

3.3 Water Absorption

Water loss from lithium tetraborate appears to be irreversible. Vacuum dried material increased in weight by only 0.5% in 6 days on exposure to normal laboratory atmosphere. Exposure to an atmosphere of 10% relative humidity for 6 days gave a weight increase of 0.1%.

It is noteworthy that the solubility of the material decreases markedly after fusion, but this aspect requires further study.

3.4 Absolute Density

Determinations carried out on the fused material, under benzene in a Specific Gravity bottle gave an average value of 2.35 g/cm^3 .

3.5 Commercially Available Material

3.5.1 Sieve Analysis of Vacuum Dried Powder

This material was received from B.D.H. Ltd. and is indicative of the size distribution obtained on drying. Drying was carried out by heating the material to 250°C for several hours in a vessel evacuated to 1 mm Hg pressure. The water removed was collected by means of a cold trap.

	+ 10	B.S.S. Mesh	0.7%
-10	+ 25	B.S.S. Mesh	24.7%
-25	+ 44	B.S.S. Mesh	9.5%
-44	+ 72	B.S.S. Mesh	9.3%
-72	+ 100	B.S.S. Mesh	7.4%
-100	+ 200	B.S.S. Mesh	16.6%
-200	+ 300	B.S.S. Mesh	8.9%
	- 300	B.S.S. Mesh	22.7%

3.5.2 Tapped Packing Density of Powder

The material as supplied was vacuum dried and then fused. Crystalline lithium tetraborate was formed on slow cooling and this was subsequently ground and size graded for the following examination:-

Tapped Packing Density

-300 B.S.S. Mesh Powder	41.0% of Absolute Density
-44 + 85 B.S.S. Mesh Powder	59.0% of Absolute Density
2 Grade Mixture	69.3% of Absolute Density
(61% - 44 + 85, 39% -300 B.S.S. Mesh)	

The comparative figure for vacuum dried material which had not been recrystallised or size graded was 30.0% of absolute density.

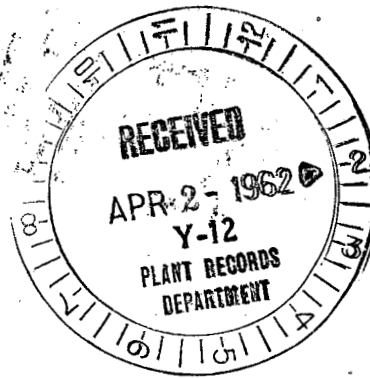
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