

THE PREPARATION, CHARACTERIZATION,
AND THERMAL BEHAVIOUR OF SOME LITHIUM ALUMINUM
OXIDES: Li_3AlO_3 AND Li_5AlO_4

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The purpose of this research was to study the best conditions for the synthesis of the double oxides Li_5AlO_4 and Li_3AlO_3 in the solid state starting from the simple oxides, and to determine their heats of formation.

Li_5AlO_4 was obtained from Li_2O or Li_2O and $\gamma\text{-Al}_2\text{O}_3$ in a Li/Al molar ratio of 5 : 1, and was characterized by X-ray methods. Lithium orthoaluminate, Li_3AlO_3 , was obtained from Li_2O and $\gamma\text{-Al}_2\text{O}_3$ in a molar ratio 3 : 1. The postulated formula, Li_3AlO_3 , was confirmed by chemical analysis.

The temperature ranges in which the compounds are stable were established by the DTA method, and were found to be very limited for Li_3AlO_3 (400–430°) but greater for Li_5AlO_4 (440 – more than 600°).

The heats of formation of Li_5AlO_4 and Li_3AlO_3 , also determined by means of the DTA method, were found to be -552.3 ± 0.8 kcal/mole and -416.8 ± 2 kcal/mole, respectively.

The number and the stabilities of the compounds formed by reaction between Li_2O and Al_2O_3 are rather uncertain; it is well known that the possibility of the formation of lithium aluminum double oxides is highly dependent on the $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio and on the firing temperature. Debray and Hardy [1], Hagemuller and Debray [2], Kordes [3], Lehmann and Hesselbarth [4], Zintl and Morawietz [5], and Hummel et al. [6] reported that the only high-temperature forms of lithium aluminum double oxides are h- LiAlO_2 (h = high-temperature modification) and LiAl_5O_8 , whereas Lehmann and Hesselbarth [7], and Torkar et al. [8] concluded that l- LiAlO_2 (low-temperature modification) and Li_5AlO_4 are the only existing low-temperature forms.

The purpose of the present work was to investigate in some detail the reactivity conditions in the solid state between aluminum oxides and lithium compounds in order to obtain pure Li–Al–O compounds and to determine the possibility of the formation of other so far unknown mixed oxides.

In particular we investigated mixtures with Li/Al molar ratios of 5 : 1 and 3 : 1 (at different firing temperatures), in order to obtain pure Li_5AlO_4 and to examine its thermal behaviour; moreover, our aim was to discover the formation conditions of other double oxides such as Li_3AlO_3 , a compound already postulated by Kröger and Fingas [9] and by Fedorov and Shamrai [10], but never characterized in its chemical and physical properties, and also to examine its thermal behaviour.

Experimental and results

Preparation

γ - Al_2O_3 , prepared by calcination at 500° of the precipitate formed from $\text{Al}(\text{NO}_3)_3$ in ammonia solution, was used as the aluminum reagent. We preferred to use γ - Al_2O_3 , instead of the α - Al_2O_3 used by several other authors, because of its higher surface area and thus its higher reactivity in the solid state; γ - Al_2O_3 was therefore a fixed component for all the preparations.

For the lithium reagent, lithium nitrate and carbonate were used in the first stage of the investigation, as suggested by several authors; however, probably due to the high temperature of decomposition of LiNO_3 and Li_2CO_3 to give Li_2O [11], the above lithium compounds did not react very easily with Al_2O_3 (many unwanted phases were observed by X-ray powder analysis). It was thus thought preferable to use highly pure Li_2O and Li_2O_2 (supplied by "LCAO" Co.) as starting materials. The reagents (Al_2O_3 and Li_2O or Li_2O_2) were mixed in a mortar in Li/Al molar ratios from 3 : 1 to 5 : 1 and each mixture was calcined in the temperature range 400 – 700° for a number of hours varying from 10 to 500. After each firing an X-ray powder spectrum was prepared for an examination of the phases present in the samples.

It was found that for the Li_5AlO_4 preparation the best firing temperature is about 500° in air. At temperatures lower than 500° , phases such as Li_2O and Al_2O_3 are still present, whereas at higher temperatures (600 – 700°) the presence of I- LiAlO_2 , Li_2O and Li_5AlO_4 is observed.

The compound was finally obtained completely pure as a fine, white powder under the following conditions: $\text{Li}_2\text{O}_2 + \gamma$ - Al_2O_3 in the molar ratio 5 : 1 at 500° in air for 140 hours. The formation of Li_5AlO_4 was also observed in the reaction of $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3$ (5 : 1) at 500° , in agreement with the findings of Lehmann and Hesselbarth [7]. It should be noted that when Li_2CO_3 or LiNO_3 were used as starting materials, a certain amount of I- LiAlO_2 was also obtained at 500° .

For the preparation of the lithium orthoaluminate, Li_3AlO_3 , as described in detail later, the best conditions were to heat a 3 : 1 Li_2O_2 – Al_2O_3 mixture at 400° in air for 500 hours.

An attempt to prepare this compound from $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3$ (at the same firing temperature, 400° , and a molar ratio 3 : 1) was unsuccessful. Using these reagents we obtained only LiAlO_2 (I-form) and Li_5AlO_4 phases.

X-ray spectra

Phases were identified by a Philips X-ray diffraction instrument using CuK_α (nickel-filtered) radiation. The X-ray patterns were taken both with a Debye–

Table 1

X-ray powder pattern of Li_5AlO_4

No.	Our data			Lehmann and Hesselbarth [7]	
	$2\theta^\circ$	d	I^a	d	I
1	17.2	5.16	w	5.21	w
2	19.8	4.48	vvw	4.48	vvw
3	22.0	4.04	s	4.07	s
4	23.2	3.83	vw	—	—
5	24.0	3.71	vs	3.74	vs
6	—	—	—	3.38	vvw
7	29.8	3.00	vvw	3.02	vvw
8	30.8	2.90	vvw	—	—
9	32.0	2.80	vvw	—	—
10	32.8	2.73	vvw	2.75	vvw
11	33.3	2.69	vw	—	—
12	34.5	2.60	vs	2.62	vs
13	35.8	2.51	vvw	2.52	vvw
14	36.1	2.49	vvw	—	—
15	37.0	2.43	vw	2.43	vw
16	37.5	2.40	vvw	—	—
17	38.1	2.36	vvw	—	—
18	39.0	2.31	vvw	—	—
19	40.5	2.23	vvw	2.26	vvw
20	42.2	2.14	vvw	2.15	vvw
21	43.5	2.08	vvw	2.08	vvw
22	46.0	1.97	vvw	1.98	vvw
23	46.5	1.95	vvw	—	—
24	47.4	1.92	w	1.93	w
25	49.3	1.85	vvw	1.87	vvw
26	50.5	1.81	vvw	—	—
27	51.4	1.78	vw	1.78	vw
28	52.7	1.74	vvw	1.75	vvw
29	54.5	1.68	vw	1.69	vw
30	55.5	1.66	vvw	1.66	vvw
31	57.4	1.61	vvw	—	—
32	57.9	1.59	s	1.61	s
33	59.0	1.57	vvw	—	—
34	60.4	1.53	vvw	1.53 ^b	vvw
35	61.1	1.52	vvw	—	—
36	63.3	1.47	vvw	1.47 ^b	vw
37	63.8	1.46	vvw	—	—
38	67.4	1.39	vvw	1.40	vvw
39	68.5	1.37	vw	1.38	vw
40	69.5	1.35	vw	1.35 ^b	w
41	70.3	1.34	vw	—	—
42	73.0	1.30	vvw	1.30	vvw
43	77.2	1.24	vw	1.24	vw
44	78.5	1.22	vvw	1.23	vvw
45	81.3	1.18	vvw	1.19	vvw

Table 1 (cont.)

Our data				Lehmann and Hesselbarth [7]	
No.	$2\theta^\circ$	d	I^a	d	I
46	84.0	1.15	vw	1.16	vw
47	85.2	1.14	vw	1.14	vw
48	87.3	1.12	vw	1.12	vw
49	89.7	1.09	vvw	1.10	vvw

^a Visually estimated intensities: vs = very strong; s = strong; w = weak; vw = very weak; vvw = very very weak.

^b Broad diffuse bands, as observed by the authors of [7].

Scherrer powder photographic camera, 114.6 mm in diameter (Straumanis mounting technique), and with a Philips powder goniometer using an angular speed of $1/4^\circ$ (2θ) per minute. The lines on the X-ray films were read visually with a Norelco measuring device and their positions corrected for film shrinkage.

Table 1 reports the values of the Bragg 2θ angles, the interplanar d spacings, and the estimated intensities I for the X-ray spectrum of the sample obtained by calcining Li_2O_2 (or Li_2O) + Al_2O_3 (5 : 1) at 500° for 140 hours, i.e. of Li_5AlO_4 . In the same Table the data reported by Lehmann and Hesselbarth [7] for Li_5AlO_4 are presented for comparison. In this product no other phases were detected, indicating that the above preparation gives a pure, uncontaminated Li_5AlO_4 compound. It should be noted that we have observed 12 very very weak reflections not reported by Lehmann and Hesselbarth: since these peaks could not be attributed to any phase other than Li_5AlO_4 we think that this difference in the spectra is probably due to a longer film exposure time applied by us. As regards the peak at $d = 3.38 \text{ \AA}$ which was observed (very very weak) by L. and H. [7] we did not detect it at all.

Characterization of the unknown phase, Li_3AlO_3

The characterization of Li_3AlO_3 was first performed by X-ray methods. Since the X-ray pattern of this compound is not available in the literature, we applied a wide range of temperature ($300-600^\circ$) for the reactions of several mixtures of lithium and aluminum oxides in a Li/Al molar ratio of 3 : 1, and the X-ray spectrum of each final product was very carefully studied.

Only in the X-ray spectrum of the $\text{Li}_2\text{O}_2 + \text{Al}_2\text{O}_3$ (3 : 1) mixture, in a firing temperature range of $400-450^\circ$, were there many X-ray lines which could not be attributed to any known phase such as Li_2O , Li_2O_2 , LiOH , $\gamma\text{-Al}_2\text{O}_3$, l- and h- LiAlO_2 , Li_5AlO_4 and LiAl_5O_8 ; the intensities of these lines decreased with increasing temperature, and their disappearance (for products heated above 450°) coincided with the appearance of reflections due to l- LiAlO_2 and Li_5AlO_4 . It was therefore inferred that the above unclassified X-ray lines belong to a new unknown phase, which is very unstable and only obtainable at temperatures around $400 \pm 20^\circ$.

Table 2

X-ray powder spectrum of the product obtained from the reaction $\text{Li}_2\text{O}_2 + \gamma\text{-Al}_2\text{O}_3$ 3 : 1, at 400° for 500 hrs. For comparison a list of the reflections (as taken from ref. [12] and from our reference spectra) is given for LiOH and $\gamma\text{-Al}_2\text{O}_3$

No.	Product			LiOH			$\gamma\text{-Al}_2\text{O}_3$		
	J^a	2θ	d	I	2θ	d	I	2θ	d
1	vw	18.95	4.683				vw	19.5	4.55
2 ^b	s	20.35	4.353	90	20.32	4.37			
3	m	21.60	4.114						
4	m	22.20	4.004						
5	m	23.25	3.826						
6	vw	28.50	3.132						
7	w	29.55	3.023						
8	m	30.60	2.921						
9	s	31.85	2.810						
10 ^b	vs	32.80	2.732	100	32.80	2.73	vw	32.4	2.76
11	m	33.45	2.679						
12	m	34.20	2.622						
13 ^b	s	35.65	2.515	70	35.48	2.53			
14	s	37.00	2.430				m	37.2	2.42
15	vw	38.15	2.359						
16	vw	39.90	2.259				m	39.7	2.27
17 ^b	vvw	41.70	2.166	40	41.62	2.17			
18	vvw	43.55	2.078						
19 ^c	s	45.60	1.998				vs	45.8	1.98
20 ^b	vw	49.15	1.857	50	49.25	1.85			
21	vw	50.35	1.812						
22 ^b	m	51.40	1.774	75	51.33	1.78	vvw	51.1	1.79
23 ^b	s	55.95	1.643	70	55.70	1.65			
				70	56.08	1.64			
24	vvw	56.90	1.618						
25	vvw	57.90	1.593						
26	vw	58.80	1.570						
27	vvw	60.00	1.542						
28	w	60.45	1.531				vw	60.7	1.53
29	vvw	61.40	1.510						
30 ^b	m	62.40	1.488	70	62.31	1.49			
31	vvw	63.60	1.463						
32	vvw	65.60	1.423						
33 ^c	w	67.00	1.397	30	67.92	1.38	s	67.0	1.397
34 ^b	vw	70.00	1.343	30	70.24	1.34			
35	vvw	71.40	1.321						
36	vw	72.83	1.298						
37 ^b	vvw	74.00	1.281	50	74.06	1.28			
38 ^b	w	75.95	1.253	60	75.45	1.26			
39	vvw	79.60	1.204	40	79.15	1.21	vvw	78.0	1.225
40	vw	85.10	1.140	50	85.10	1.14	w	87.4	1.144
41	vw	86.45	1.126	40	87.00	1.12			
42	vw	92.40	1.068	20	92.20	1.07			
43	vw	95.80	1.039	40	95.65	1.04			

Table 2 (cont.)

No.	Product			LiOH			γ -Al ₂ O ₃		
	I ^a	2 θ	d	I	2 θ	d	I	2 θ	d
44	vvw	99.00	1.014				vvw	97.5	1.025
45	vvw	100.10	1.006						
46	w	101.30	0.997	50	101.15	0.998			
47 ^c	vw	103.40	0.982				vvw	102.5	0.988
48	w	106.80	0.960	45	106.50	0.962			
49	vw	109.20	0.946						
50 ^c	vw	113.60	0.922				vvw	112.5	0.930
51 ^d	vvw	118.70	0.895	35	118.50	0.897			
52	w	120.60	0.887	50	120.50	0.888			
53	vvw	124.80	0.869				vvw	122.0	0.881
54	w	131.60	0.844						
55	vw	148.60	0.800				w	145.0	0.808
56	w	152.10	0.794						
57	m	161.40	0.781						

^a Visually estimated intensities: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; vvw = very very weak.

^b Dotted lines.

^c Broad, diffuse bands.

^d Well-resolved α_1 - α_2 doublets on the film; the positions of α_1 lines were measured from line No. 51 on.

The X-ray spectrum of the product obtained by reaction of Li₂O₂ + Al₂O₃ at 400° for 500 hours was therefore carefully investigated. Table 2 shows that the main phases after heating consisted exclusively of the new compound and a certain amount of LiOH and Al₂O₃. These unreacted phases were easily recognizable since those corresponding to LiOH are shown in the X-ray powder film as characteristic dotted lines whilst those belonging to Al₂O₃ appear as broad, diffuse bands.

The presence of phases such as Li₂O₂, Li₂O, l-LiAlO₂, Li₅AlO₄ and LiAl₅O₈ in the above product was definitely excluded since their corresponding strongest X-ray lines were not revealed on the X-ray pattern, even at longer film exposures.

Table 3 reports the lines taken from Table 2, excluding those corresponding to LiOH and Al₂O₃, and considering only those belonging to the new phase.

Moreover, the X-ray powder pattern of Li₃BO₃, as taken from ASTM cards [12], is reported in the same Table in order to show the similarity of its spectrum with that of Li₃AlO₃.

Analysis

The analyses for lithium and aluminum were performed by means of the atomic absorption technique, using an "Optica" instrument, and also by flame photometry (Li), using an "EEL" apparatus.

Table 3
X-ray patterns of Li_5AlO_3 and Li_3BO_3

No. ^a	Li_5AlO_3			Li_3BO_3 ^c			
	<i>I</i> ^b	2θ	<i>d</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1	vw	18.95	4.683	4.59	6	1.386	3
3	m	21.60	4.114	4.09	15	1.361	3
4	m	22.20	4.004	3.99	10	1.336	4
5	m	23.25	3.826	3.74	3	1.299	3
6	vw	28.50	3.132	3.20	8	1.262	3
7	w	29.55	3.023	3.03	100	1.189	3
8	m	30.60	2.921	2.867	20		
9	s	31.85	2.810	2.675	50		
11	m	33.45	2.679	2.625	55		
12	m	34.20	2.622	2.450	6		
14	s	37.00	2.430	2.395	4		
15	vw	38.15	2.359	2.344	40		
16	vw	39.90	2.259	2.315	10		
18	vw	43.55	2.078	2.295	10		
21	vw	50.35	1.812	2.265	2		
24	vw	56.90	1.618	2.238	3		
25	vw	57.90	1.593	2.214	8		
26	vw	58.80	1.570	2.069	3		
27	vw	60.00	1.542	2.040	5		
28	w	60.45	1.531	1.996	10		
29	vw	61.40	1.510	1.895	6		
31	vw	63.60	1.463	1.866	25		
32	vw	65.60	1.423	1.845	4		
35	vw	71.40	1.321	1.777	8		
36	vw	72.85	1.298	1.758	3		
44	vw	99.00	1.014	1.630	5		
45	vw	100.10	1.006	1.608	20		
54	w	131.60	0.844	1.591	10		
56	w	152.10	0.794	1.561	5		
57	m	161.40	0.781	1.535	6		
				1.463	4		
				1.440	5		
				1.408	3		

^a Numbers correspond to those in Table 2.

^b Visually estimated intensities: s = strong; m = medium; w = weak; vw = very weak; vvw = very very weak.

^c From refs. [12] and [15].

Li_5AlO_4 (in the pure state as tested by X-ray diffraction) was completely dissolved in acidified (HCl) water and found to contain 27.9% of lithium and 21.3% of aluminum (the calculated values for the Li_5AlO_4 formula, M.W. = 125.67, are 27.61 and 21.46%, respectively). The above experimental percentages thus correspond to a Li/Al molar ratio of 5.08, in good agreement with the expected value of 5.0.

It should be remembered that the product obtained by the reaction of $\text{Li}_2\text{O}_2 + \text{Al}_2\text{O}_3$ (3 : 1) at 400° for 500 hrs contains the unknown lithium aluminum double oxide as well as some unreacted LiOH and Al_2O_3 . To find the effective Li/Al molar ratio of the new compound contained in this mixture the following procedure was followed:

a) since only the Al_2O_3 is insoluble in acidified (HCl) water, its percentage was found by weighing the residue remaining after washing repeatedly and centrifuging the powder;

b) the solution (containing the lithium aluminum double oxide and the unreacted LiOH) was analyzed and found to contain 22% and 15% by weight of Li and Al , respectively;

c) since only the LiOH was found to be soluble in ethyl alcohol, the alcoholic solution (containing the LiOH) was analyzed and found to contain 10.3% of Li .

The effective percentages contained in the lithium aluminum compound were therefore $22 - 10.3 = 11.7\%$ of Li , and 15% of Al , thus giving a Li/Al molar ratio of 3.03, in good agreement with the value of 3.0 expected for the formula Li_3AlO_3 (M.W. = 95.79, calculated $\text{Li}\% = 21.74$ and $\text{Al}\% = 28.16$).

Thermal behaviour

For the differential thermal analysis (DTA) a Netzsch apparatus was used (DDK measuring head platinum containers, Pt-PtRh 10% thermocouples, and a heating rate of $5^\circ/\text{min}$). Heated kaolin was used as the reference material. All DTA curves were obtained using about 100 mg of undiluted samples, in an air atmosphere.

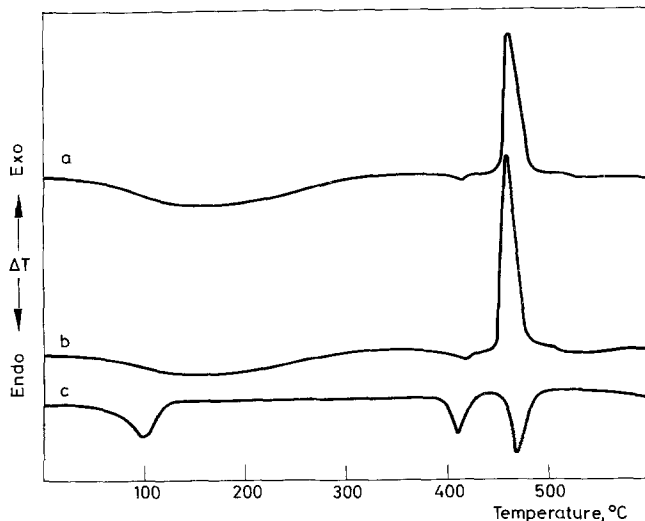


Fig. 1. *a*: DTA curve of the mixture $\text{Li}_2\text{O} + \gamma\text{-Al}_2\text{O}_3$ 3 : 1; *b*: DTA curve of the mixture $\text{Li}_2\text{O} + \gamma\text{-Al}_2\text{O}_3$ 5 : 1; *c*: DTA curve of Li_2O alone

It should be noted that the determinations of the heats of formation of Li_5AlO_4 and Li_3AlO_3 were performed by the DTA method since: a) the compounds are very hygroscopic and this could lead to large errors in the measurements of ΔH_0 by the usual solution calorimeters; and b) after detection of the peaks by the DTA method, an immediate X-ray test on the powder can check that the above compounds were really formed.

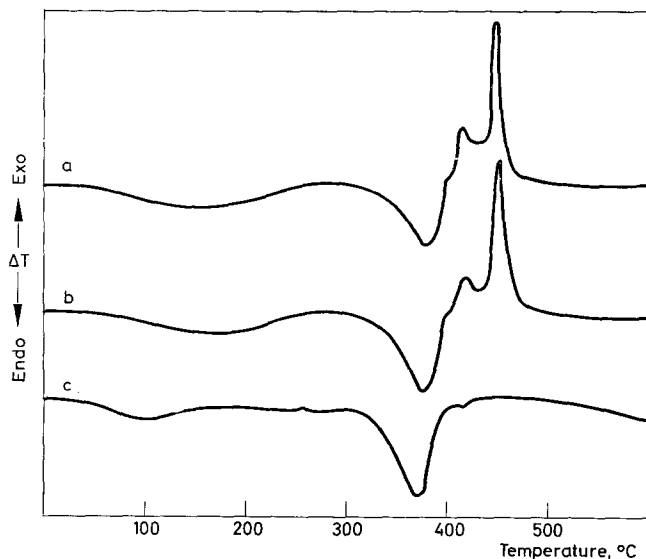


Fig. 2. *a*: DTA curve of the mixture $\text{Li}_2\text{O}_2 + \gamma\text{-Al}_2\text{O}_3$ 3 : 1; *b*: DTA curve of the mixture $\text{Li}_2\text{O}_2 + \gamma\text{-Al}_2\text{O}_3$ 5 : 1; *c*: DTA curve of Li_2O_2 alone

The DTA curves corresponding to the $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3$ mixtures in the ratios 3 : 1 and 5 : 1 show (Fig. 1a and 1b) only one sharp exothermic peak in the range $450\text{--}530^\circ$, due to the formation of the compound Li_5AlO_4 , as confirmed by the X-ray pattern.

The DTA curves corresponding to the $\text{Li}_2\text{O}_2 + \text{Al}_2\text{O}_3$ mixtures in the ratios 3 : 1 and 5 : 1 (Figs 2a and 2b) show an endothermic peak at $320\text{--}380^\circ$ due to the decomposition of Li_2O_2 into Li_2O and $1/2 \text{O}_2$ (confirmed by the DTA curve of pure Li_2O_2 , Fig. 2c), and two exothermic peaks in the ranges $400\text{--}440^\circ$ and $450\text{--}510^\circ$, respectively. The first one is due to the formation of Li_3AlO_3 , the second to that of Li_5AlO_4 .

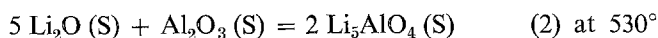
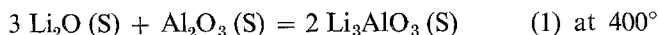
The appearance of only one exothermic peak in the range $450\text{--}530^\circ$ (Fig. 1a and 1b) by mixing Li_2O and Al_2O_3 in Li/Al molar ratios 3 : 1 or 5 : 1 shows that under these conditions only Li_5AlO_4 is formed. The presence of a weak endothermic peak at $400\text{--}425^\circ$ in these curves led us to suppose that, under the described operational conditions of sampling, Li_2O did not remain uncontaminated, and this was not surprising considering the well-known ready tendency of Li_2O

to react with water and carbon dioxide in air. This supposition was further confirmed by the DTA curve of Li_2O alone (Fig. 1c), and from its X-ray spectrum; since the latter showed the presence of LiOH and Li_2CO_3 (in small quantities) together with the main Li_2O phase, the two endothermic peaks in the range $400-500^\circ$ of the DTA curve in Fig. 1c are therefore due to the melting of LiOH (the DTA curve of LiOH alone shows only one endothermic reaction at $400-430^\circ$, exothermic in the cooling curve in the range $400-380^\circ$) and to the initial decomposition of Li_2CO_3 (which in fact starts to decompose over 440° , respectively [11]).

It is therefore reasonable to infer that the presence of surface LiOH and Li_2CO_3 hinders the reactivity of Li_2O with Al_2O_3 up to 450° and thus prevents the formation of Li_3AlO_3 . Only at 450° can uncontaminated Li_2O react with Al_2O_3 to give Li_5AlO_4 and LiAlO_2 (at $\text{Li}/\text{Al} = 3 : 1$), or Li_5AlO_4 alone (at $\text{Li}/\text{Al} = 5 : 1$), as observed by X-ray powder spectra.

In contrast, when Li_2O_2 is used as reactant (Fig. 2) two exothermic peaks are always observed; the peak at $400-440^\circ$ is more consistent if the Li/Al ratio is $3 : 1$. It is evident that in this case the conditions are more favourable for the formation of Li_3AlO_3 , and that this compound is an intermediate in the Li_5AlO_4 formation from $5 : 1$ mixtures. It may be assumed that Li_3AlO_3 is formed only by Li_2O_2 because the temperature of complete decomposition of Li_2O_2 to give $\text{Li}_2\text{O} + \frac{1}{2} \text{O}_2$ almost coincides with the temperature of formation of Li_3AlO_3 , and Li_2O_2 is thus a sure source of uncontaminated Li_2O . It should be noted that the smooth and large endothermic peaks observed in all the DTA curves of Li_2O or $\text{Li}_2\text{O}_2 + \text{Al}_2\text{O}_3$ in the temperature range $120-250^\circ$ are probably due to the dehydration of Al_2O_3 , which was believed to contain 10% water.

The experimental determination of the heats of formation of the compounds synthesized here was based on the direct calorimetric measurement of the heats of reactions in the solid state from the constituents, the heats of formation of the starting oxides being known from the literature in the temperature range where the reactions



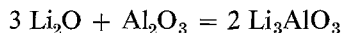
occur. The values of the heats of reaction ΔH (1) and ΔH (2) were obtained from the areas of the well-defined exothermic peaks observed in the DTA curves.

The apparatus was previously calibrated in the same temperature range with compounds of known heats of fusion, such as CsNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$.

For Li_3AlO_3 the heating of $\text{Li}_2\text{O}_2 + \text{Al}_2\text{O}_3$ mixtures in a molar ratio of $3 : 1$ was halted at 440° , after the formation of the product and before the start of its decomposition into Li_5AlO_4 and LiAlO_2 . The amount of Li_3AlO_3 formed was derived from the weight of unreacted Al_2O_3 ; in fact the amount of alumina not dissolved in HCl ($1 : 8$) with respect to the alumina initially weighed gives the

amount of product formed. In the calculation it was also considered that the Al_2O_3 used contained (as observed experimentally) about 10% water.

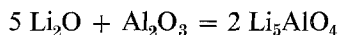
The heat of reaction (1):



averaged from four different runs, was found to be -16.5 ± 2 kcal/mole. By using the heats of formation at 400° of Li_2O (-138.55 kcal/mole) [13] and of $\gamma\text{-Al}_2\text{O}_3$ (-384.84 kcal/mole) [14], the measured heat of reaction (1), -16.5 ± 2 kcal/mole, corresponds to a calculated heat of formation of Li_3AlO_3 of -416.75 ± 2 kcal/mole at 400° .

The determination of the heat of formation of Li_5AlO_4 was performed in the same way by weighing the area of the exothermic peak obtained from the reaction of $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3$ (5 : 1) at 470° .

The heat of reaction (2):



was in quite good agreement irrespective of the lithium oxide used and was found to be -13.5 ± 0.8 kcal/mole (average of five runs with both types of mixture). By using the same values of the heats of formation of Li_2O and $\gamma\text{-Al}_2\text{O}_3$ as for reaction (1), the measured heat of reaction (2), -13.5 ± 0.8 kcal/mole, leads to a calculated heat of formation of Li_5AlO_4 of -552.3 ± 0.8 kcal/mole at 500° .

Discussion

The results of our investigation clearly indicate that the formation of some lithium aluminum oxides, such as Li_3AlO_3 and Li_5AlO_4 , depends on a very limited range of physical variables. As usual when reactivity conditions are investigated, we have varied the type of starting materials, the composition range of the reagents, as well as the temperature of reaction.

It has been found that Li_5AlO_4 may be prepared in a pure form by calcining a mixture of Li_2O_2 and $\gamma\text{-Al}_2\text{O}_3$ in a molar ratio of 5 : 1 at 500° in air for several hours (140), as well as by reaction between $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3$. In contrast, if Li_2CO_3 or LiNO_3 are used as starting lithium reagents, phases other than Li_5AlO_4 are formed. The Li_5AlO_4 phase is stable in the temperature range $450\text{--}650^\circ$; above 650° small amounts of other phases, such as 1-LiAlO_2 , are revealed by X-ray spectra. This range of stability was observed when lithium oxides were used as reagents; when Li_2CO_3 or LiNO_3 are used the upper limit of stability is lowered.

However, it is much more difficult to prepare Li_3AlO_3 ; until now, in fact, this compound was unknown, its existence only having been postulated by a few authors [9, 10]. We have found that it can be formed during the reaction in the solid state between Li_2O (obtained during the decomposition of the initial

Li_2O_2) and $\gamma\text{-Al}_2\text{O}_3$ (a very reactive form of alumina due to its high surface area), with a Li/Al molar ratio of 3 : 1, and in a very narrow range of temperature, namely at $400 \pm 20^\circ$ in air; above this temperature it decomposes giving the meta-aluminate, LiAlO_2 and Li_5AlO_4 . Moreover, it is formed only by reaction of lithium peroxide with alumina, since attempts to prepare it from lithium oxide, lithium carbonate or lithium nitrate were unsuccessful.

The formation of Li_3AlO_3 by the reaction in the solid state between Li_2O_2 and Al_2O_3 (3 : 1) at 400° for 500 hrs has been confirmed by chemical analysis and X-ray spectra. However, both chemical analyses and X-ray spectra have shown that the reaction is not complete, since the powder, even after prolonged heating (500 hrs), still contains a certain amount (about 40%) of unreacted materials such as LiOH and Al_2O_3 .

It is very interesting to note that the spectrum of this compound is very similar to that of Li_3BO_3 [15] (one of the two types reported in the literature for this compound [12]). Table 3 shows a clear correlation between the first lines of Li_3AlO_3 characterized here and of Li_3BO_3 studied by Sastry and Hummel [15]; the d values show a special agreement with one another and it is therefore suggested that the two compounds are almost similar with respect to their crystal symmetries, unit cells and structures. The two compounds have very similar formulas, and should give, if they are isomorphous (as the similarity of their X-ray spectra suggests), the formation of solid solutions.

It should finally be noted that the temperature of formation found here for Li_3AlO_3 is rather different from that observed (500°) by Kröger and Fingas [9].

The heats of formation of Li_3AlO_3 and Li_5AlO_4 have been calculated from DTA curves, as stated above, to be -416.75 ± 2 and -552 ± 0.8 kcal/mole, respectively.

The DTA curves have also confirmed the observations from the numerous attempts at calcination, and have made it possible to define the stabilities of the various phases formed during the reaction, and to understand the different reactivities with respect to Al_2O_3 of the several lithium compounds used in the preparation.

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RÉSUMÉ — On a recherché les meilleures conditions pour réaliser la synthèse à l'état solide des oxydes doubles Li_5AlO_4 et Li_3AlO_3 en partant des oxydes individuels et pour déterminer leur chaleur de formation. Li_5AlO_4 a été obtenu en partant de Li_2O_2 (ou Li_2O) et de $\gamma\text{-Al}_2\text{O}_3$ dans le rapport molaire $\text{Li}/\text{Al} = 5/1$; il a été caractérisé par étude aux rayons X. L'orthoaluminate de lithium, Li_3AlO_3 , a été obtenu en partant de Li_2O_2 et de $\gamma\text{-Al}_2\text{O}_3$ mélangés dans le rapport 3/1. L'analyse chimique a confirmé la formule présumée Li_3AlO_3 . L'ATD a permis de déterminer le domaine de stabilité thermique de ces composés: très restreint pour Li_3AlO_3 (400—430°), plus grand pour Li_5AlO_4 (440—plus de 600°), ainsi que leurs chaleurs de formation: -416.8 ± 2 kcal/mole et -552.3 ± 0.8 kcal/mole, respectivement.

ZUSAMMENFASSUNG — Es wurden die Bildungsverhältnisse der doppelten Oxide Li_5AlO_4 und Li_3AlO_3 in fester Phase ausgehend von den einfachen Oxyden geprüft und ihre Bildungswärmen bestimmt. Li_5AlO_4 wurde aus Li_2O_2 oder Li_2O und $\gamma\text{-Al}_2\text{O}_3$ beim Molverhältnis von Li/Al 5 : 1 erhalten und röntgenographisch identifiziert. Das Orthoaluminate Li_3AlO_3 erhielt man beim Molverhältnis 3 : 1 von Li_2O_2 und $\gamma\text{-Al}_2\text{O}_3$. Die Zusammensetzung von Li_3AlO_3 wurde durch chemische Analyse nachgewiesen. Die DTA-Prüfung zeigte, daß Li_3AlO_3 nur im sehr kleinen Temperaturgebiet (400—430°), Li_5AlO_4 hingegen im weiteren Bereich zwischen 440—600° stabil ist. Die Bildungswärmen betragen für Li_5AlO_4 -552.3 ± 0.8 , für Li_3AlO_3 -416.8 ± 2 kcal/Mol.

Резюме — Цель исследования — поиск наилучших условий синтеза двойных окисей Li_5AlO_4 и Li_3AlO_3 в твердой фазе на основе простых окисей и определение теплот их образования. Li_5AlO_4 получен из Li_2O_2 или Li_2O и $\gamma\text{-Al}_2\text{O}_3$ при молярном соотношении Li/Al 5 : 1, и его структура подтверждена рентгенодифракционным методом. Ортоалюминат лития, Li_3AlO_3 , получен из Li_2O_2 и $\gamma\text{-Al}_2\text{O}_3$ при молярном соотношении 3 : 1. Предполагаемая формула подтверждена химическим анализом. Методом ДТА установлено, что область температур, в которой эти соединения стабильны, довольно ограничена для Li_3AlO_3 (400—430 °С) и более широкая для Li_5AlO_4 (440 — \leq 600 °С). Теплоты образования Li_5AlO_4 и Li_3AlO_3 также определены с помощью метода ДТА и составляют 552.3 ± 0.8 и 416.8 ± 2 Ккал/мол, соответственно.