ARPA Order No. 306-62
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SEMIANNUAL TECHNICAL SUMMARY REPORT

FOR

HYDROTHERMAL GROWTH OF CRYSTALS OF $LaAlO_3$

31 December 1964 to 1 July 1965
NONR-4616(00)

Submitted by:
Airtron, a division of Litton Industries
200 East Hanover Avenue
Morris Plains, New Jersey

OFFICE OF NAVAL RESEARCH
NONR-4616(00)
ADVANCED RESEARCH PROJECTS AGENCY
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This research is a part of Project DEFENDER, sponsored by Advanced Research Projects Agency, Department of Defense, and technically monitored by the Office of Naval Research, under Contract NONR-4616(00).

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

I. PURPOSE

Our primary objective is to grow large single crystals of $LaAlO_3$ doped with Cr from a hydrothermal system, using seed crystals produced from a molten salt system. Factors influencing the growth of large single crystals such as regions of congruent solubility, crystal stability, and degree of solubility will be examined.

II. ABSTRACT

Large crystals of $LaAlO_3$ have been successfully grown from a straight PbF_2 flux. However, soak temperatures above 1400°C are required for solution of LaF_3 formed by the reaction of La_2O_3 and PbF_2. These high temperatures result in premature failure of the furnace and platinum container. PbF_2 was, therefore, abandoned and a search was initiated to modify the PbF_2 flux, or to find a more suitable solvent. Among the solvents investigated were PbO-PbF_2, BaO and Bi_2O_3, all with small additions of B_2O_3. Results are encouraging.

The regions of phase stability have been determined for $LaAlO_3$ and $La(OH)_3$ under hydrothermal conditions. From this data it is apparent that in order to operate in a region where $LaAlO_3$ is the only stable solid and to stay below the 435°C transition temperature, the solvent concentrations must be <2 or >7 m K_2CO_3. The composition of the fluid was analyzed quantitatively for alumina and lanthana content. Although the data show considerable scatter, they are in agreement with and have confirmed the observed crystallization of solid $La(OH)_3$. In the large crystal growth autoclaves, spontaneous nucleation of $LaAlO_3$ in the growth chamber has been obtained from a nutrient composed of powdered La_2O_3 and flame fusion ruby pieces. The physiochemical nature of the nutrient has added to the difficulty of calculating a correct fill. Only seven runs have been made thus far.

III. STAT[illegible]

This report covers the six-month period December 31, 1964, through July 1, 1965. Table I indicates the completed goals set forth at the beginning of this Contract and the current status of u[illegible]ompleted ones. The most serious delays were caused by the necessity to explore new solvent systems because of the inability to grow $LaAlO_3$ from PbF_2 f[illegible]uxes below 1400°C, and the delivery of autoclaves which failed to hold the hydrothermal system because of faulty construction.

TABLE I

STATUS

Item	Goal	Purpose	Current Status	Problems Encountered or Expected	Original Estimated Completion Date	New Estimated Completion Date
1	Equipment preparation & material procurement	Provide equipment & materials for crystal growth experiments	Complete	None	9/64	-----
2	Study to determine hydrothermal solvent suitable for $LaAlO_3$ recrystallization below 435°C	Growth of $LaAlO_3$ below 435°C	Complete	None	10/64	-----
3	Study to determine flux from which seed crystals can be grown	Solvent selection	Complete	Insoluble LaF_3 produced with PbF_2 solvent	11/64	-----
4	Determine solubility of $LaAlO_3$ in hydrothermal solvent	Solubility curve	Change to phase diagram determination	Stable $La(OH)_3$ phase	1/65	5/65
5	Determine solubility of $LaAlO_3$ in PbF_2 solvent	Solubility curve	Complete	Stable LaF_3 phase	2/65	6/65
6	Optimize growth conditions for large, high quality molten salt seed crystals	Provide large seed crystals	In progress	Stable LaF_3 phase requires use of new solvent systems	3/65	10/65
7	Determine effect of temperature, pressure and ΔT on hydrothermal growth of $LaAlO_3$ crystals	Growth of large hydrothermal crystals	In progress	--------	4/65	10/65
8	Determination of effect of seed orientation and quality on hydrothermal crystal quality	Growth of high quality hydrothermal $LaAlO_3$	Not started	High quality seed crystals	-----	6/66
9	Grow large $LaAlO_3$ crystals hydrothermally	Contract objective	Not started	None	8/65	8/66
10	Lifetime measurements	Contract objective	Not started	None	8/65	8/66
11	Write Final Report	Contract requirement	Not started	None	9/65	9/66

IV. MOLTEN SALT EFFORT

A. Crystal Growth

A summary of all molten salt runs is shown in Table II.

An attempt was made to optimize growth conditions for the growth of large seed crystals. All the runs up to this point had been made in 250 ml crucibles, and all had been too slushy to pour, even at 1300°C. It was felt that perhaps this was due to high evaporation rates of PbF_2 in small crucibles and too much solute.

The first run in the 5 1/4 inch can, where evaporation is only about 1 percent, was No. 34. (See Table II). In this run, 22 m percent La_2O_3 and 22 m percent Al_2O_3 were heated to 1300°C with PbF_2 as solvent. At the 1000°C pour temperature, once again, the solution was a slushy mass with a few $LaAlO_3$ plates on the surface.

It has been planned to explore a higher crystallization temperature range. Run No. 35 gave us the opportunity to explore the 1200 to 1500°C range. This run, with about two and one-half times as much total material as No. 34, was soaked with the pedestal reading 1300°C and the plug at 1400°C. The purpose of the large difference was to encourage the $LaAlO_3$ to crystallize on the bottom of the can instead of on the surface of the melt as is usually the case. A defective controller caused a more rapid cooldown than had been programmed, and the temperature at the pedestal was raised to 1400°C for one hour in order to redissolve any crystals that had been formed. The plug temperature was at 1500°C during this soak

TABLE II

Run No.	Units	La_2O_3	Al_2O_3	Cr_2O_3	PbF_2	PbO	Bi_2O_3	BaO	B_2O_3	Total	Purpose of Run	Furnace Used	Crucible Used	Soak Temperature Pedestal (°C)	Soak Temperature Plug (°C)	Soak Time (hours)	Cooling Rate (°C/hour)	Pour Temperature Selected	Remarks
34	grams moles m %	1013.4 3.110 22.10	317.1 3.109 22.09	0.0	1925.0 8.055 50.00	0.0	0.0	0.0	56.9 0.812 5.81	3312.4 14.071 100.00	Crystal growth	4"	5 1/4"	1300	----	2	2	1000°C	Very small pour, very few crystals on top of mushy flux.
35	grams moles m %	2532.9 7.778 22.20	793.1 7.778 22.11	0.0	8540.0 34.884 49.98	0.0	0.0	0.0	182.2 2.963 5.81	7779.3 36.177 100.00	Crystal growth	4"	5 1/4"	1300	1400	1	2	1200°C	Raised pedestal temperature to 1400°C, plug to 1500°C for 1 hour. Good pour at 1200°C and about 100 grams of crystals grew.
36		Not Run																	--------
37	grams moles m %	90.0 0.276 23.49	30.0 0.294 25.04	0.0	0.0	0.0	300.0 0.605 51.49	0.0	0.0	420.0 1.175 100.00	Test Bi_2O_3 as a solvent	3"	250 ml	1300	----	2	10	1000°C	Good clear small crystals about 1 mm². No pour.
38	grams moles m %	2020.9 6.209 22.18	634.8 6.224 22.24	0.0	3438.0 14.026 50.00	0.0	0.0	0.0	113.0 1.623 5.77	6223.5 28.116 100.00	Effect of high ΔT on crystal growth	4"	5 1/4"	1317	1450	2	0.5	1200°C	Good pour. Some clear crystals. Incomplete solution.
39	grams moles m %	2020.9 6.219 22.16	634.8 6.214 22.14	0.0	3436.0 14.066 50.00	0.0	0.0	0.0	113.0 1.623 5.77	6223.9 28.112 100.00	Increased soak temperature	4"	5 1/4"	1400	1500	4	0.5	1200°C	Good pour. 45 grams of clear crystals. Good yield. Evidence of very slight incomplete solution.
40		[illegible]																	--------
41	grams moles m %	130.0 0.400 22.09	45.5 0.446 22.09	0.08 0.0002 0.009	245.2 1.000 50.00	0.0	0.0	0.0	8.9 0.128 5.82	455.82 2.205 100.00	Cr doped crystals	3"	250 ml	1400	----	6	2.0	1400°C	No pour, slushy, yellow-white flux. Good crystal growth.
42a	grams moles m %	130.0 0.400 21.40	49.5 0.486 25.40	0.0	245.7 1.000 53.09	0.0	0.0	0.0	0.0	475.2 1.872 100.00	Solubility determination	1"	250 ml	1400	----	1	10	1350°C	No pour.
42b 1 & 2	grams moles m %	60.0 0.145 6.15	32.5 0.323 9.20	0.0	245.7 1.000 81.72	0.0	0.0	0.0	0.0	338.2 1.346 100.00	Solubility determination	(1) 1" (2) 3"	(1) 250 ml (2) 250 ml	(1) 1300 (2) 1300	--- ----	4 1	15 10	1060°C 1090°C	(1) Large slushy mass, small liquid phase. (2) Large slushy mass, small liquid phase.
42c	grams moles m %	79.2 0.243 15.10	25.0 0.245 15.45	0.0	245.7 1.000 69.47	0.0	0.0	0.0	0.0	371.9 1.500 100.00	Solubility determination	3"	250 ml	1400	1400	2	10	1210°C	No pour, no crystals.
43	grams moles m %	0.0	0.0	0.0	100.0 0.408 47.66	100.0 0.448 52.34	0.0	0.0	0.0	200.0 0.856 100.00	X-ray standard	3"	250 ml	1100	----	1	10	1000°C	--------
44	grams moles m %	1384.4 4.611 14.16	467.8 4.588 14.09	0.38 0.0025 0.009	5434.5 20.947 64.24	0.0	0.0	0.0	170.1 2.443 7.50	7571.1 32.592 100.00	Reduced solute concentration & Cr doping	6"	5 1/4"	1400	1450	4	--	------	Run failed when platinum can leaked.
45	grams moles m %	40.0 0.123 4.03	12.5 0.123 4.03	0.0	519.4 2.400 89.94	0.0	0.0	0.0	0.5	594.9 2.446 100.00	Solubility determination	6"	450 ml	1400	---	1/2	--	------	Run failed when platinum can leaked.
46	grams moles m %	79.2 0.243 15.40	25.0 0.245 14.43	0.0	269.7 1.100 69.87	0.0	0.0	0.0	0.0	373.9 1.588 100.00	Effect of sealed can on solubility	3"	250 ml	1400	----	2	15	1125°C	No pour, no crystals.
47	grams moles m %	2502.5 4.666 14.14	467.8 4.588 14.09	0.38 0.003 0.009	6438.2 20.927 64.25	0.0	0.0	0.0	170.1 2.443 7.50	7571.9 32.572 100.00	Reduced solute concentration & Cr doping	6"	5 1/4"	1400	1450	4	0.5	1100°C	Run failed when platinum can leaked.
48		See Table III																	--------
49	grams moles m %	171.4 1.00 50.00	122.4 1.20 40.00	0.36 0.0012 0.02	0.0	0.0	0.0	0.0	0.0	511.7 2.400 100.02	Solubility sintering	--	-----	---	----	--	--	------	Sent out for sintering.
50 1 & 2	grams moles m %	40.0 0.124 9.05	30.7 0.301 8.80	0.0	404.4 1.650 81.12	0.0	0.0	0.0	12.1 0.017 0.66	499.4 2.014 100.01	Solubility determination	1"	250 ml	1400	----	24	15	1040°C	Crucible of 50-1 stuck in furnace. 50-2 was removed 24 hours later. No pour, no crystals.
51	grams moles m %	1501.4 4.611 14.16	475.8 4.666 14.09	0.0	5111.1 20.921 64.25	0.0	0.0	0.0	170.1 2.443 7.50	7474.5 32.509 100.00	Solubility & Add'l Soak 1400°C	6"	5 1/4"	1355	1400	50	1	1200°C	Very small pour, no crystals.
52	grams moles m %	90.0 0.276 3.14	30.0 0.294 1.05	0.0	0.0	0.0	0.0	300.0 1.956 52.48	89.7 1.411 35.77	509.7 3.717 100.00	Solvent selection	3"	250 ml	1300	----	16	45	1000°C	C[illegible] came off. Some spillage. Very dirty flux.
53	grams moles m %	90.0 0.276 14.06	30.0 0.294 14.91	0.0	181.1 0.738 37.48	166.1 0.780 39.90	0.0	0.0	10.0 0.144 0.66	488.0 2.334 100.00	Solvent selection	3"	250 ml	1300	----	6	5	860°C	Many small clear crystals similar to results using pure PbO.
54	grams moles m %	90.0 0.276 17.49	30.0 0.294 18.31	0.0	0.0	0.0	300.0 0.605 37.67	0.0	30.0 0.431 26.94	450.0 1.606 100.00	Solvent selection	3"	450 ml	1300	----	16	30	1000°C	Very small clear crystals, but cover came off crucible.
55	grams moles m %	45.0 0.138 10.45	15.0 0.147 11.11	0.0	0.0	0.0	300.0 0.605 45.80	0.0	30.0 0.431 32.65	390.0 1.321 100.01	Solvent selection	3"	450 ml	1300	---	16	10	1000°C	No crystals.
56	grams moles m %	0.0	0.0	0.0	0.0	0.0	0.0	400.0 1.950 61.37	65.7 1.231 38.63	465.7 3.187 100.00	Solvent preparation	3"	250 ml	1300	----	4	--	1175°C	White clean pour. Residue very dirty.
57	grams moles m %	90.0 0.276 17.19	30.0 0.294 18.31	0.0	0.0	0.0	300.0 0.605 37.67	0.0	30.0 0.431 26.84	450.0 1.606 100.01	Solvent selection	3"	250 ml	1300	----	8	3	500°C	Controller failed. Clear 0.5 cm crystals on surface of melt. No pour.
58	grams moles m %	90.0 0.276 12.97	30.0 0.294 13.82	0.0	50.0 0.204 9.59	300.0 1.344 63.16	0.0	0.0	10.0 0.014 0.66	480.0 2.132 100.00	Solvent selection	3"	250 ml	1300	----	16	5	850°C	Small pour under thick crust. Many small crystals.
59	grams moles m %	90.0 0.276 17.19	30.0 0.294 18.33	0.0	0.0	0.0	300.0 0.605 37.62	0.0	30.0 0.431 26.86	450.0 1.606 100.01	Solvent selection	3"	250 ml	1300	----	16	2	1000°C	Incomplete solution.
60	grams moles m %	90.0 0.276 11.97	30.0 0.294 12.88	0.0	0.0	450.0 1.476 58.04	150.0 0.322 13.88	0.0	30.0 0.431 18.81	750.0 2.298 100.00	Solvent selection	3"	250 ml	1300	----	16	2	500°C	Timer failed, cooled rapidly. No pour and no crystals.
61	grams moles m %	90.0 0.276 17.19	30.0 0.294 18.31	0.0	0.0	0.0	300.0 0.605 37.67	0.0	30.0 0.431 26.84	450.0 1.606 100.01	Solvent selection	3"	250 ml	1300	----	16	2	970°C	No pour. Square growing $LaAlO_3$ crystals on surface of flux covered with flat plates of yellow material.

Molten Salt Effort (continued)

period and with the rotation of the melt it can be assumed that the temperature in the crucible was 1450°C, or higher. When the crucible was removed at 1200°C after a 2°C per hour cooldown, the usually slushy melt was absent. Instead, a thin crust of $LaAlO_3$ had formed over the surface of the melt, which, when broken, revealed a perfectly liquid flux, which was easily poured. About 100 grams of $LaAlO_3$ had formed on the walls and base of the can, of much better quality than any grown previously. It was not immediately apparent whether the increased quality of the crystals and the fluid melt were caused by the higher temperatures, the temperature gradient or the reduced solvent evaporation caused by the crust, which covered the surface. Two additional runs were made, Run No. 38 with a ΔT of 140°C with a pedestal soak temperature of only 1300°C, and Run No. 39 with a 1400°C pedestal soak temperature and a ΔT of 100°C. Run No. 38 with the lower soak temperature had better quality growth than No. 39 and liquid flux under the crust, but there was still some evidence of incomplete solution because most of the crystals were bunched together at the center of the base of the can. The soak period of two hours used for No. 38 was increased to 4 hours for No. 39 and the soak temperature raised from 1300°C to 1400°C with a ΔT of 100°C. The result was the highest yield yet obtained, 430 grams, with good quality crystals of a size suitable for hydrothermal seeds obtained from about 10 percent of the yield, see Figure 1. One rod measuring 0.121" x 0.910" grew completely free of flux inclusions.

Figure 1

Molten Salt $LaAlO_3$ Crystals

Molten Salt Effort (continued)

Three explanations for the sudden increase in quality and yield of $LaAlO_3$ in Run No. 39 are possible:

1. The crust, which formed over the melt in 5 1/4 inch cans somehow prevented oxide formation or evaporation from taking place to the same extent as in the 250 ml crucibles. The obvious test of this theory was a run in a sealed platinum can.

2. The 44 m percent solute concentration was simply too great for solution below 1400°C. The test of this theory was to repeat Run No. 39 with 50 percent less solute at a 1300°C soak temperature.

3. The formation of insoluble LaF_3 by the reaction of La_2O_3 and PbF_2 in the melt prevented the formation of $LaAlO_3$. The LaF_3 did not dissolve completely until soak temperatures in excess of about 1450°C were reached. The test of this theory was the same as under No. 2 above.

Run No. 46 was used to test theory No. 1. A platinum can measuring about 3 inches long by 2 1/2 inches wide was filled with only 15 m percent La_2O_3 and 15 m percent Al_2O_3, with 69 m percent PbF_2 added as flux. The cover was carefully welded on and the crucible inserted into a 3 inch furnace maintained at 1400°C. There was no ΔT, and a 2 hour soak period was programmed followed by a 15°C cooling rate. The crucible was removed at 1250°C. The cover was quickly punched open with a can opener. There was no liquid phase. When the cover was removed, there were no crystals of $LaAlO_3$.

Runs 44 and 47 were two attempts to test theory No. 2. Unfortunately,

Molten Salt Effort (continued)

an attempt was made to produce Cr doped crystals as a by-product of these experiments. Both platinum cans failed due to corrosion, apparently caused by reduction of PbO to metallic lead when Cr^{3+} was oxidized to Cr^{6+}. This reaction apparently occurs quite readily in lead salts. A third attempt without Cr, Run No. 51, was successfully completed. In this run, 14 m percent La_2O_3 and Al_2O_3, respectively, were added to 64 m percent PbF_2 and 7.5 m percent B_2O_3. The crucible was soaked at a pedestal temperature of 1350°C and a plug temperature of 1400°C for 50 hours, then slowly cooled to 1200°C at the rate of 1°C per hour. When opened, there was virtually no liquid phase and no crystals. These two experiments and Run No. 39 essentially proved proposition No. 3 and a detailed analysis of this mechanism may be found in the Discussion Section of this report.

One major problem exists, however, in the production of crystals at such high temperatures from molten PbF_2. Furnace life and platinum crucible life are drastically reduced at 1500°C and above. Every time a furnace was used at greater than 1400°C it had to be completely rebuilt. Even 1350°C reduces the lifetime of the furnace. So severe was the furnace attack, in fact, that a search for a new solvent system was started in spite of the success which had been achieved with PbF_2.

B. Solvent System Investigation

Pure PbO was the original solvent used by Remeika[1] in the synthesis of $LaAlO_3$. This solvent resulted in only very small crystals and proved to be

Molten Salt Effort (continued)

very corrosive to platinum particularly when Cr^{3+} was used. In the light of our previous experience, three solvents suggested themselves:

1. $PbO-PbF_2-B_2O_3$

This solvent, which is a modification of pure PbF_2, appeared attractive because of the $PbO-PbF_2$ eutectic at 500°C. It has been used successfully for the growth of YIG[2] and YAG.[3]

Run No. 53, with about 13 m percent La_2O_3 and Al_2O_3, respectively, was heated to 1300°C with a $PbO-PbF_2-B_2O_3$ mixture of 37, 35 and 0.6 m percent, respectively. The crystals produced when the run was poured at 840°C were small, clear crystals, similar to those that grow in pure PbO. In addition, LaF_3 was present. It was necessary to go to quite high PbO values to prevent LaF_3 production. Run No. 58 was made with 9 m percent PbF_2 and 63 m percent PbO, in order to minimize LaF_3 production. Again, only very small $LaAlO_3$ crystals were grown.

2. $BaO-B_2O_3$

This solvent has been used for the growth of YIG.[4] It contained no Pb, so corrosion of platinum should be absent. It has a low vapor pressure so evaporation is not a problem.

Run No. 52 used 7 m percent La_2O_3 and Al_2O_3, respectively, in 52 m percent BaO and 33 m percent B_2O_3 in a 250 ml beaker. Unfortunately, the BaO appeared to be very impure. No crystals of $LaAlO_3$ grew and the flux had a dirty violet appearance. An attempt to purify this flux by premelting with-

Molten Salt Effort (continued)

out solute and decanting the pure liquid was only partially successful. BaO_2 which is available in reagent grade was tried next, but no crystals were found in the melt.

3. Bi_2O_3-B_2O_3

This solvent has been used to grow $GaFeO_3$.[5] Run No. 54 consisted of 17 and 18 m percent La_2O_3 and Al_2O_3, respectively, with 38 m percent Bi_2O_3 and 27 m percent B_2O_3 as flux. The crystals produced were very small but clear, and very little solvent poured off at the 1070° pour temperature. The run was repeated, No. 55, with a lower solute concentration of 10 and 11 m percent La_2O_3 and Al_2O_3 in 46 m percent Bi_2O_3 and 33 m percent B_2O_3. No crystals grew from this composition, so the composition and conditions of No. 54 were repeated as Run No. 57. In this case, the photocell failed in the West controller, causing a rapid cooldown to 500°C, but good $LaAlO_3$ crystal growth on the surface of the solidified melt was obtained. A third run, No. 61 identical to No. 57, also produced crystals of $LaAlO_3$. These crystals measure approximately 5 x 5 x 3 mm and are light-green or gray and of fair quality.

The Bi_2O_3-B_2O_3 solvent thus appears to be the best solvent found thus far. It has a eutectic at 622°C, low volatility and is not corrosive. An attempt will be made to optimize growth conditions using this solvent.

C. Solubility of $LaAlO_3$ in PbF_2

Although we have abandoned PbF_2 as a solvent for $LaAlO_3$, con-

Molten Salt Effort (continued)

siderable work was done in an effort to obtain phase equilibrium data in the PbF_2-La_2O_3-Al_2O_3 system. We present this work since it may be of help to workers in the field dealing with related systems.

Molten salt solubility techniques used successfully with ruby are obviously not applicable to $LaAlO_3$ grown in PbF_2 systems, because of the formation of insoluble LaF_3. Only those runs in which this phase has been dissolved and $LaAlO_3$ crystallizes can be used for solubility determinations. Run No. 39 was such a run (see Table II). The flux from this run, which was poured at 1200°C was analyzed chemically and by X-ray diffraction. The wet analysis indicated 21.88 wt percent $LaAlO_3$ and 16.28 wt percent LaF_3 in the flux at the 1200°C quench temperature. The estimate obtained by X-ray diffraction was 20 wt percent $LaAlO_3$.

Solubility determinations utilizing the loss in weight of $LaAlO_3$ crystals immersed in PbF_2 in sealed platinum tubes were stymied by two factors. One was the high percentage of leaks in the sealed tubes at low, as well as high temperatures. The other was the very high apparent solubility values obtained because the $LaAlO_3$ crystals formed LaF_3 when dissolved in PbF_2. A summary of all weight loss solubility runs may be found in Table III.

The tubes were crimped in a 3 jaw chuck and welded closed with an electric arc. It was found that equilibrium was achieved in 48 hours. At the quench temperature, they were dropped into a bucket of water. Those

TABLE III

Run No.	Wt. of Solvent (gms)	Wt. of Nutrient (grams) Before	Wt. of Nutrient (grams) After	Change in Nutrient Wt. (gms)	Wt. of Sealed Capsule (grams) Before	Wt. of Sealed Capsule (grams) After	Capsule Size (in.)	Temperature	Solvent	Nutrient	Duration of Soak (hrs.)	Did Capsule Leak	% Solubility Δ nut. wt. x 100 / Solvent Wt.
1	1.4040	0.5555	0.1570	0.3985	4.0267	4.0107	1.5	1207°C	Pb_2OF_2	$LaAlO_3$	60	yes	28.38
2	1.2528	0.5185	0.0817	0.4369	3.8161	3.7979	1.5	1207°C	Pb_2OF_2	$LaAlO_3$	60	yes	34.87
3	0.9592	0.7113	0.5747	0.1366	3.7074	3.6920	1.5	1207°C	Pb_2OF_2	$LaAlO_3$	44	no	14.24
4	1.2243	0.5027	0.1917	0.3110	3.7918	3.9618	1.5	1207°C	Pb_2OF_2	$LaAlO_3$	20	yes	25.40
5	1.5158	0.8515	0.0000	<0.8515	4.3424	3.2320	1.5	1200°C	PbF_2	$LaAlO_3$	24	yes	<56.17
6	1.5230	0.6260	0.0000	<0.6260	4.2430	4.1557	1.5	1200°C	PbF_2	$LaAlO_3$	24	no	<41.10
7	1.8008	0.5073	0.0000	<0.5073	4.3916	4.3850	1.5	1200°C	PbF_2	$LaAlO_3$	24	no	<28.17
8	1.5875	0.7433	0.0000	<0.7433	4.4211	3.2198	1.5	1200°C	PbF_2	$LaAlO_3$	24	yes	<46.82
9	0.9307	0.3960	0.0000	<0.3960	3.3816	3.3445	1.5	1200°C	PbF_2	LaF_3	24	no	<42.55
10	1.3646	0.4571	0.0000	<0.4571	3.8879	3.8511	1.5	1200°C	PbF_2	LaF_3	24	no	<33.50
11	1.2282	0.4859	0.0000	<0.4859	3.7750	3.8216	1.5	1200°C	Pb_2OF_2	LaF_3	24	yes	<39.56
12	1.2186	0.4505	0.0000	<0.4505	3.7130	3.6523	1.5	1200°C	Pb_2OF_2	LaF_3	24	yes	<36.97
13	0.8131	1.2716	0.0135	1.2581	------	------	1.5	1100°C	PbF_2	$LaAlO_3$	48	yes	154.73
14	0.9499	0.8159	0.0010	0.8149	------	------	1.5	1100°C	PbF_2	$LaAlO_3$	48	yes	85.79
15	0.8008	1.1742	0.0610	1.1132	------	------	1.5	1100°C	PbF_2	$LaAlO_3$	48	yes	139.01
16	0.8461	1.2988	0.0135	1.2853	------	------	1.5	1100°C	PbF_2	$LaAlO_3$	48	yes	151.91
17	1.0510	1.3167	0.4244	0.8923	4.4769	4.5601	1.5	1200°C	PbF_2	$LaAlO_3$	72	yes	84.90
18	0.6521	1.1991	0.7046	0.4945	3.9252	3.9200	1.5	1200°C	PbF_2	$LaAlO_3$	72	no	75.83
19	0.8908	1.2465	0.6458	0.6027	4.2049	4.1848	1.5	1200°C	PbF_2	$LaAlO_3$	72	yes	67.66
20	0.9177	1.5439	0.2401	1.3038	8.1195	7.2280	4	1200°C	PbF_2	$LaAlO_3$	72	yes	142.07
21	0.8908	1.9468	0.0000	<1.9468	8.5745	9.8226	4	1200°C	PbF_2	$LaAlO_3$	72	yes	<218.55
22	0.8687	1.7910	0.0000	<1.7910	8.2823	9.2805	4	1200°C	PbF_2	$LaAlO_3$	72	yes	<206.17
23	0.9227	1.8554	0.0243	1.8311	8.3904	9.4330	4	1000°C	PbF_2	$LaAlO_3$	72	yes	198.56
24	0.8841	1.9733	0.0067	1.9666	8.5871	8.5804	4	1000°C	PbF_2	$LaAlO_3$	72	no	222.44
25	0.9227	1.9556	0.5739	1.3817	8.4120	9.1136	4	1000°C	PbF_2	$LaAlO_3$	72	yes	149.75
26	2.3809	------	------	------	------	------	4	1000°C	PbF_2	PbF	72	no	------
27	1.4723	2.1006	0.0000	<2.1006	------	------	4	1000°C	PbF_2	$LaAlO_3$	72	no	<142.67
28	1.7660	1.0555	0.8847	0.1708	------	------	4	1000°C	PbF_2	Al_2O_3	72	no	9.67
29	1.6531	1.0326	0.0000	<1.0326	8.1878	8.1650	4	1000°C	PbF_2	La_2O_3	72	no	<62.00

Molten Salt Effort (continued)

that had water inside when they were opened were presumed to have leaked. Some that were dry inside, but showed large weight changes, were considered to have leaked also. Seventy-two percent showed evidence of leaks. Several corrections were made in the tubes and welding procedure.

1. Tubes were increased in length from 1 1/2 inches to 4 inches long.

2. Tubes were filled to less than one-half total length and the remaining volume was flattened before sealing.

3. The crimping procedure in the 3 jaw chuck was abandoned in favor of welding the flattened top of a tube folding over 1/8 inches and welding again. When this latter procedure was used for Nos. 26, 27, 28, and 29, all remained leak-free.

Solubility values varied widely; however, even in the tubes that did not leak at 1200°C, for example, Run No. 18, gave a value of 75.83 percent, yet at 1000°C, Run No. 24 gave a value of 222.44 percent, and No. 27 was greater than 142.67 percent. The reason for the wide variation of solubility values is not known, but there is an indication of retrograde solubility. A run with sapphire, instead of $LaAlO_3$ at 1000°C, gave a value of 9.67 percent vs. 10.01 wt. percent reported by Giess, using a similar technique. The values are close enough together to indicate that the technique is being duplicated. A new series using the new sealing method, but with Bi_2O_3 as the solvent, will be started soon.

Molten Salt Effort (continued)

D. Chromium Doping

Several runs were made in order to grow $LaAlO_3$ crystals with Cr^{3+}. Run No. 41 contained 0.009 m percent Cr_2O_3 in the melt. The crystals were a deep red and fluoresced very weakly under 3660A mercury radiation. Corrosion of the crucible was not excessive. The same percentage of Cr in two 5 1/2 inch cans, Nos. 44 and 47, led to premature failure of the platinum can when only a slightly higher soak temperature than the 1400°C used with No. 41 was employed.

E. Discussion

The major constituent found in the solidified melts in the PbF_2-Al_2O_3-La_2O_3 system is LaF_3. Also detected are $PbAl_2O_4$ and PbO as well as some PbF_2. It is obvious that two reactions take place during the heat up and soak stages:

$$3\ PbF_2 + La_2O_3 \rightarrow 2\ LaF_3 \downarrow + 3\ PbO \qquad (1)$$

$$PbO + Al_2O_3 \rightarrow PbAl_2O_4 \qquad (2)$$

It appears that LaF_3 solubility in the PbO that results from the double decomposition reaction of (1) is quite low, below 1400°C. The small yield of $LaAlO_3$ crystals usually found as a thin crust on the surface of the melt along with a few cubes of $LaAlO_3$, (see Figure 2), is a result of this limited solubility. As the soak temperature approaches the melting point of LaF_3 which is 1493°C, however, a rapid increase in solubility occurs. Just what the exact mechanism is that results in the formation of $LaAlO_3$

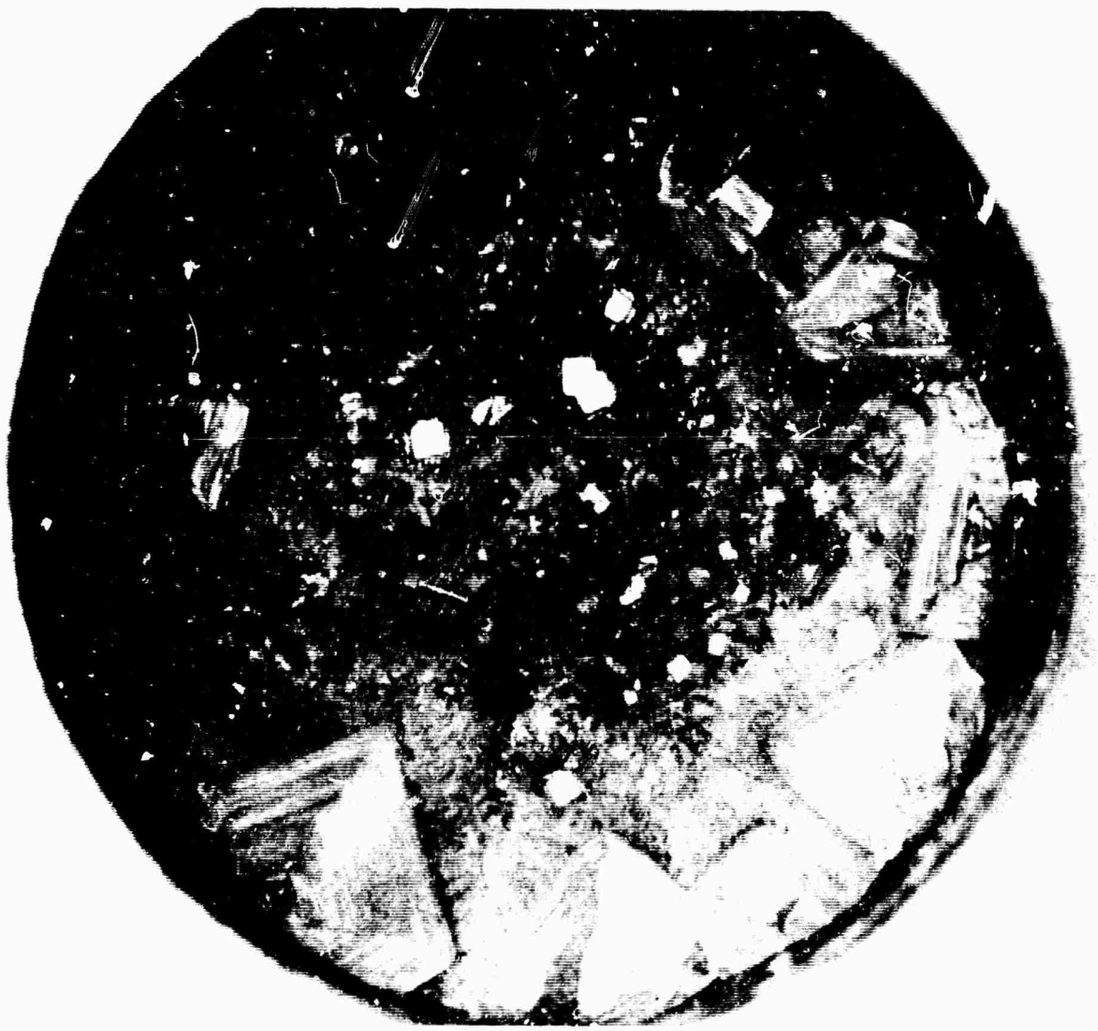

Figure 2

Photograph of Crucible with Crystals Attached

Molten Salt Effort (continued)

crystals upon cooling from a soak temperature of 1500°C is not known, but the reactions:

$$LaF_3 + PbAl_2O_4 \rightarrow LaAlO_3 + AlF_3 \uparrow + PbO \quad (3)$$

$$3\ PbF_2 + La_2O_3 + Al_2O_3 \xrightarrow{1500°C} LaAlO_3 + LaF_3 + AlF_3 \uparrow + 3\ PbO \quad (4)$$

offer an explanation, probably oversimplified, of what takes place in solution during crystal growth. An analysis of the crystals and flux from No. 39 reveals that of 12.44 m La and 12.45 m Al in the original composition, 10.18 m La could be accounted for in the flux and crystals after the run and only 6.65 m Al. The weight loss which took place during the run, 2 pounds 10 ounces, could be accounted for largely by the combined loss of AlF_3 = 487 gms and LaF_3 = 431 gms. Further evidence of AlF_3 formation and sublimation was obtained from a similar analysis of Run No. 41, which was heated to only 1400°C. In this case, 0.167 m La and 0.347 m Al remained out of a total 0.972 m each. The loss of AlF_3 was less at lower temperatures.

If equipment were available which would enable crystal growth at temperatures of 1500°C, it appears that PbF_2 would be a satisfactory solvent for the growth of $LaAlO_3$.

In view of the above, solubility experiments using either the sealed tube or fluxed melt techniques must be soaked at 1500°C in order to dissolve all the LaF_3 formed. The value of 22 wt. percent $LaAlO_3$ for Run No. 39 which was soaked near 1500°C probably comes close to an accurate value for $LaAlO_3$ solubility in this system at 1200°C.

V. HYDROTHERMAL EFFORT

A. Tem-Pres Studies

1. Phase Studies

The major effort during the past half year has been expended on projects utilizing the Tem-Pres apparatus.

A wide-range program was carried out to outline the P, T, and solvent concentration regions of stability for $LaAlO_3$ and $La(OH)_3$ especially in the areas below the reported transition temperature (435°C). The stability of $LaAlO_3$ was studied as a function of temperature and K_2CO_3 concentration at a constant pressure of 20,000 psi. The results are shown in Figure 3. Note that the $LaAlO_3$ field narrows with decreasing temperature. It appears that at 400°C, K_2CO_3 concentrations of less than 2 molal are required if the pressure is 20,000 psi.

Data were also acquired to determine the stability dependence of $LaAlO_3$ on pressure. Tem-Pres runs made at 400°C and at different pressures and K_2CO_3 concentrations are shown in Figure 4. Run duration varied from 24 to 64 hours. It was found that 24 hours was sufficient to assure equilibrium The stability field of $LaAlO_3$ apparently has a minimum in it at about 5 m K_2CO_3 and 5,000 psi. Over 150 data points have been collected to date in order to provide information on phase equilibria and/or fluid composition.

In order to select the best solvent concentration and to investigate the composition of the hydrothermal solutions in greater detail, we have attempted to obtain more quantitative data from the hydrothermal solutions

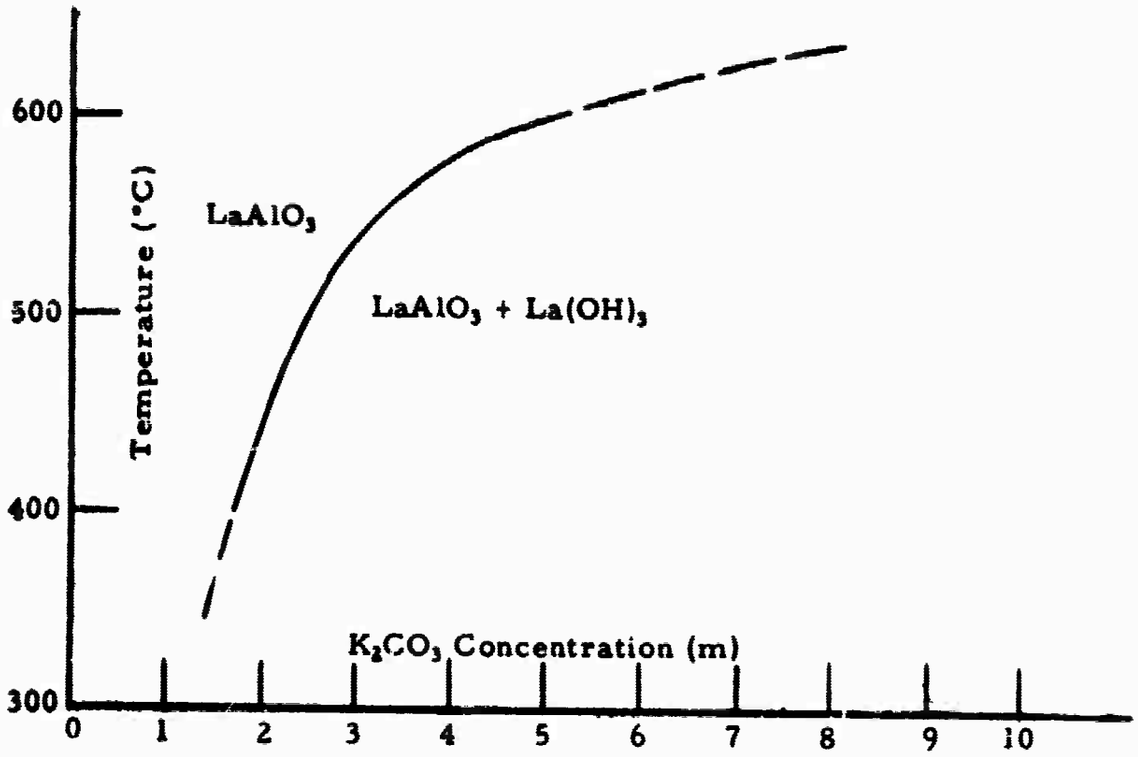

Figure 3

Solid Phase Present at 20,000 psi

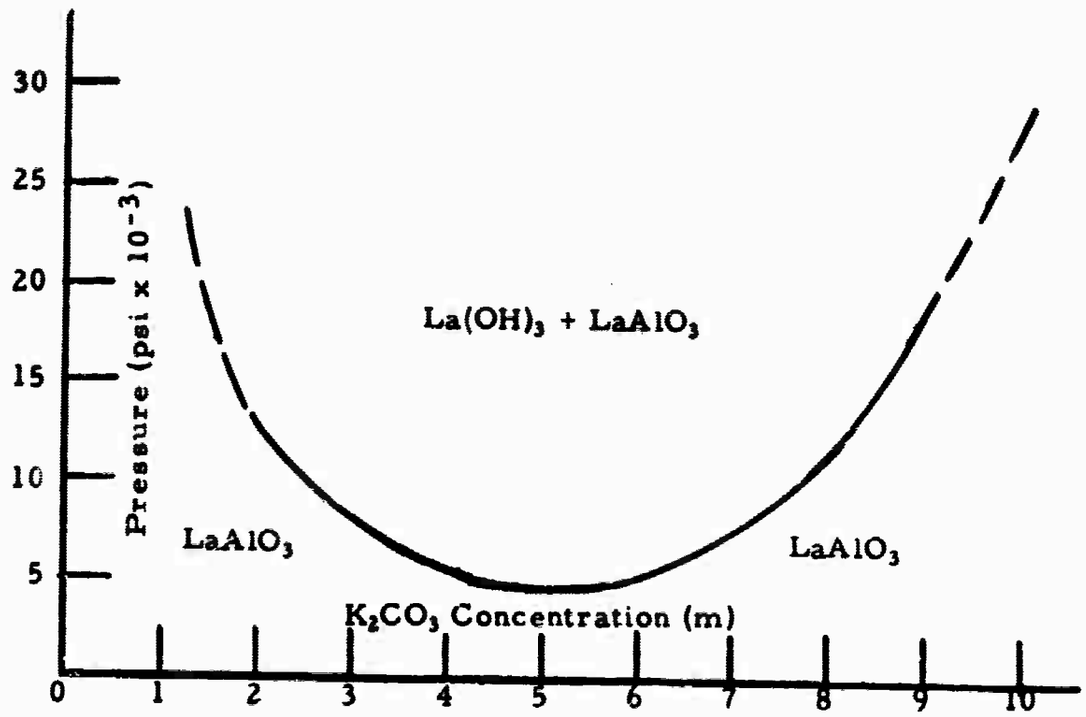

Figure 4

Solid Phase Present at 400°C

Hydrothermal Effort (continued)

by analyzing the contents in the following fashion:

A hypodermic needle (20 gauge x 1 1/2 inches long) is inserted into the quenched capsule and the liquid contents are withdrawn into the attached syringe. Generally the capsule is severely deformed after removal from the hydrothermal environment, preventing ready insertion of the needle. To avoid this difficulty, the capsules are expanded back to their original volume by a heat treatment. The interior of the capsule is purged of all water soluble materials and any fine precipitates by repeated injections and withdrawals of deionized water.

Analysis for total aluminum and lanthanum is performed on the collected rinsings and a calculation of their concentrations in the original hydrothermal fluid is made.

Accurate results depend upon assumptions that:

1. The quenching rate is great enough to produce the required finely divided gelatinous precipitate or suspension.

2. Negligible crystallization occurs on existing solids.

3. The gelatinous matter is entirely removed by the rinsing technique.

4. The solids present at quenching are well formed crystals too large to be withdrawn by the hypodermic needle.

The work has been difficult since only about 0.6 grams of solvent are used per capsule. Assuming even a very high apparent solubility of

Hydrothermal Effort (continued)

ten percent, this would mean the total solute available for analysis is only 60 mg which can be considered composed of La_2O_3 and Al_2O_3. The separation and analysis for each constituent must be carried out and related to the change of a hydrothermal variable, which would have less than a 10 percent effect. As a result, the data show scattering, some of which are shown in Figure 5. These data have been smoothed out and are presented in Figure 6. Note that the solid lines representing Al_2O_3 and La_2O_3 do not diverge greatly from stoichiometry, the mole percent ratio being 1.1 to 1.2. The lower molar solubility for La_2O_3 is in agreement with the appearance of $La(OH)_3$ as a solid phase separating out as the solvent concentration increases.

2. Crystal Growth

Crystal growth attempts at 400°C in the Tem-Pres has been plagued by the almost constant appearance of $La(OH)_3$ in the high pressure form. Lanthanum hydroxide crystals form on the seed surface and grow outward from it. A typical example of $La(OH)_3$ crystals growing on a $LaAlO_3$ seed is shown in Figure 7. Growth of the $La(OH)_3$ is caused by an incongruent solubility condition which brings about a much higher ratio of aluminum to lanthanum in solution than the ratio of aluminum to lanthanum in $LaAlO_3$. Therefore, as the system is warmed up, $LaAlO_3$ dissolves until the solution is saturated with respect to lanthanum at this point. However, the solution is still far below saturation with respect to aluminum. Selective dissolution of aluminum takes place at the surface of the $LaAlO_3$ crystal causing super-

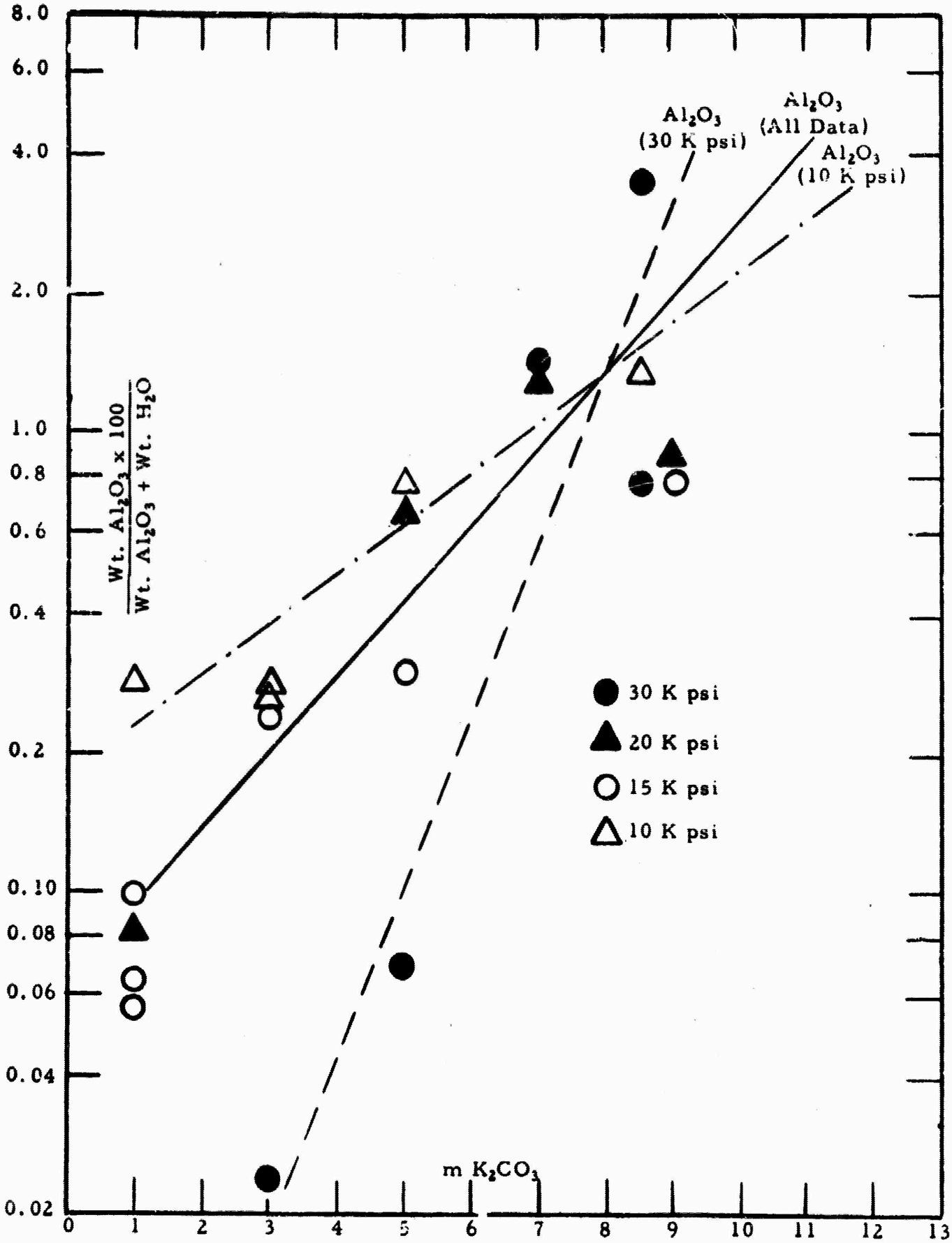

Figure 5

Al_2O_3 Solubility Data as a Function of K_2CO_3 Molality at 400°C

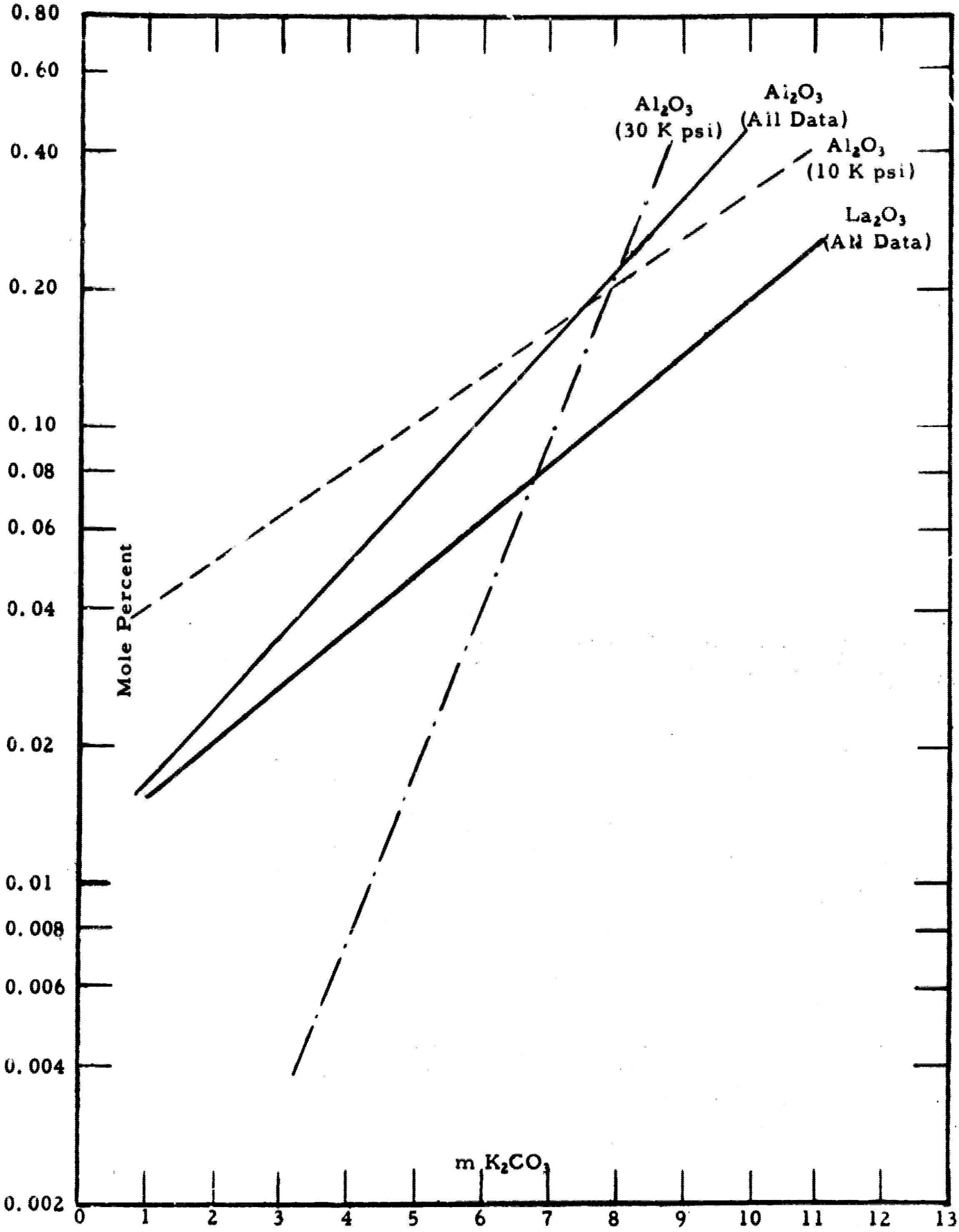

Figure 6

Mole Percent La_2O_3 and Al_2O_3 Solubility in K_2CO_3 as a Function of Molality at 400°C

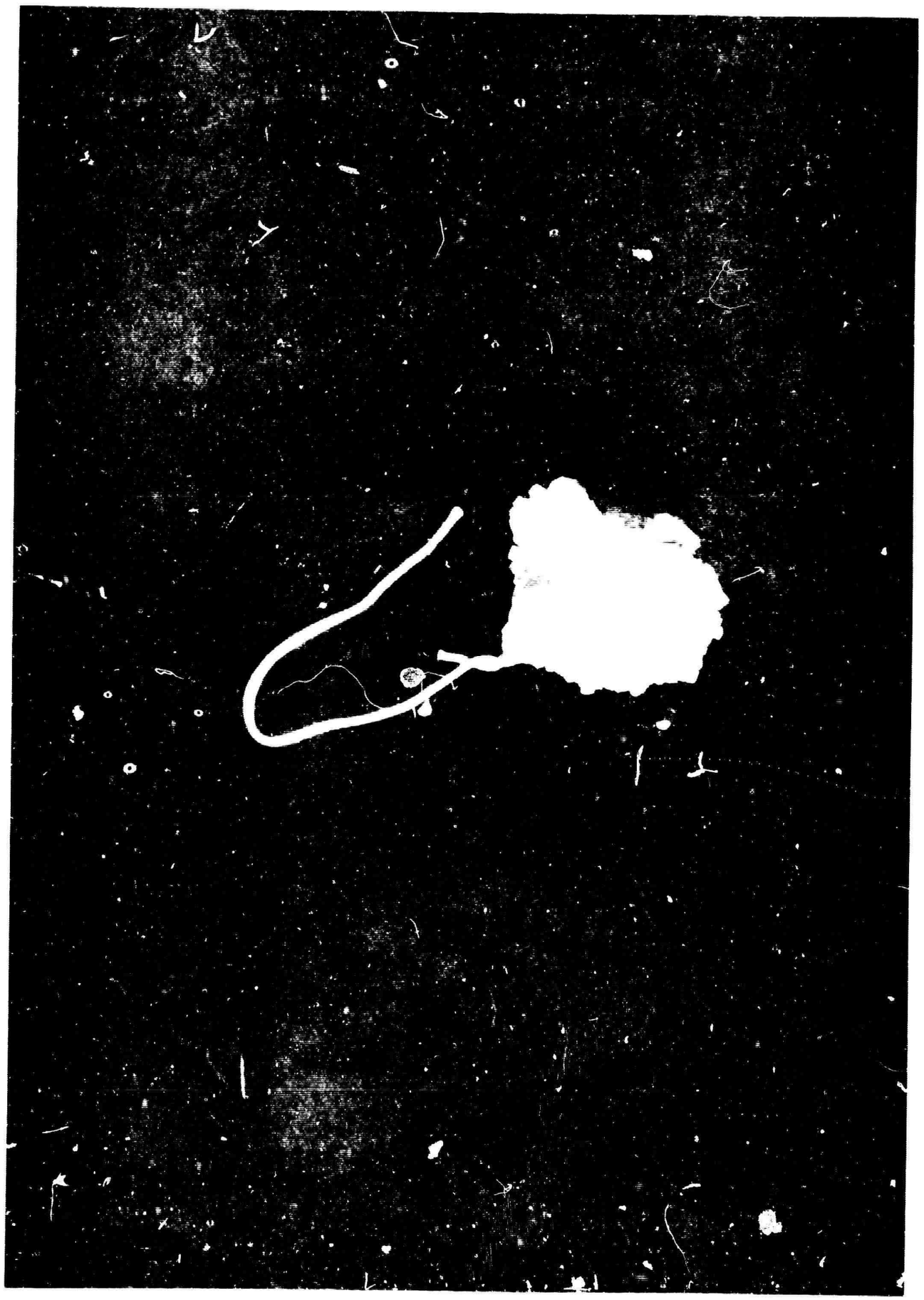

Figure 7

Hydrothermal Crystals Showing Spontaneous Nucleation Coating of $La(OH)_3$

Hydrothermal Effort (continued)

saturation and subsequent nucleation of lanthanum as $La(OH)_3$. The process is continued until the solution solubility requirements are satisfied or the $LaAlO_3$ surface is "sealed off" by $La(OH)_3$ crystals. Deposition of $La(OH)_3$ can only be a temporary effect since it is caused by the incongruent solubility condition, but nonetheless it is a very serious condition. High quality seeds could be completely covered by $La(OH)_3$ deposition.

B. Large Autoclaves

Very little progress has been made in the area of large crystal growth. This is mainly due to autoclave problems. A three month delivery time plus improper fabrication of the seal parts by the manufacturer have caused unexpected delays in the growth of large crystals. Upon their receipt, a careful examination of the autoclaves by Airtron revealed faulty machining of the critical sealing surfaces. Upon the manufacturer's insistence, Airtron tested the vessels hydrothermally. Both seals failed, one at 4,000 psi and 350°C and the other at 13,000 psi and 450°C; whereas, the manufacturer's rating is 30,000 psi at 593°C.

The manufacturer has since remachined, tested, and returned both vessels. Airtron, in turn, retested both vessels and found them to be satisfactory. They are both being used routinely at the present time.

Seven large $LaAlO_3$ crystal growth runs have been completed as of June 30, 1965. Most of the runs were made in vessels of the same size purchased under Contract AF 33(657)-10508 for the hydrothermal growth of ruby.

Hydrothermal Effort (continued)

C. Large Crystal Growth Runs

The first problem that arose in conjunction with large crystal growth runs was the lack of an adequate supply of $LaAlO_3$ nutrient. A mixture of crushed flame fusion ruby and powdered La_2O_3 was tried as nutrient in Run La-1. Operating conditions were 9,000 psi with a growth temperature of 475°C and a dissolution temperature of 528°C. Solvent was 7 molal K_2CO_3.

For the first run an estimate of the internal fill required to produce the P-T conditions desired was made. Our first approximation was 80 percent internal fill with a 60 percent external fill to produce an estimated 10,000 psi at an average temperature of 425°C.

Actual operating conditions produced a pressure of 9,000 psi but at an average temperature of 495°C or 70°C higher than estimated. It was obvious that the percent internal fill must be increased considerably in order to achieve 10,000 psi at 425°C average temperature.

The seeds dissolved during the run, but all the ruby and La_2O_3 had reacted to form $LaAlO_3$ as verified by X-ray diffraction analysis. The recovered $LaAlO_3$ had a grey-green color with an octahedral habit. Some portions of the nutrient material fluoresced orange under ultraviolet light. The fluorescent portions were excised from the nutrient and X-ray analysis was made. The material which was white and crumbly was found to be $LaAlO_3$. The source of the fluorescence has not yet been determined, but is probably a rare earth impurity in the La_2O_3.

Hydrothermal Effort (continued)

However, the fact that the mixture did react hydrothermally to produce $LaAlO_3$, provided an interim source of nutrient (though not entirely suitable) until the nutrient problem is solved. Armed with a reliable source of nutrient, a series of runs were planned to determine fill conditions for pressure balance and, if possible, obtain crystal growth and/or spontaneous nucleation.

Seal leakage forced termination of Run No. La-2 before any data could be obtained.

The planned conditions for La-3 were the same as for La-1; that is, 425°C average temperature, 10,000 psi with 7 m K_2CO_3. Internal fill was adjusted to 90 percent and external fill to 65 percent as compared to 80 percent and 60 percent previously. Actual P-T conditions achieved were 14,000 psi at 422°C average temperature or 10,000 psi at 403°C average temperature. Equilibrium conditions were at 15,000 psi, 405°C growth temperature and 468°C dissolution temperature.

All seeds were dissolved completely as in the previous run but a heavy deposit of $La(OH)_3$ was found on the wall and lid of the silver can. This deposit is expected from the phase data presented in Figures 2 and 3.

For the next run, (La-4), conditions within the region of $LaAlO_3$ stability were selected from the phase diagram to provide a region for crystallization that would be free of $La(OH)_3$ contamination. A percent fill was selected by extrapolating prior data to the P-T range desired. The ability to predict a

Hydrothermal Effort (continued)

P-T relationship from a value of percent fill increases rapidly as the number of trials becomes larger. A relatively small number of runs can be made at differing fills which will provide data points which can be interpolated or extrapolated with reasonable accuracy.

The selected conditions were 10,000 psi at 450°C average temperature to be produced by an 85 percent internal fill of 7 m K_2CO_3. Actual data recorded an average temperature of 453°C at 10,000 psi. Conditions throughout the run averaged 11,000 psi with a growth temperature of 437°C and a dissolution temperature of 496°C.

Again all seeds dissolved but there was a large amount of spontaneously nucleated $LaAlO_3$ deposited on the can walls and seed rack. Verification of $LaAlO_3$ was accomplished by X-ray diffraction analysis. The X-ray pattern and the morphology of the spontaneously deposited crystals were the same as the reacted nutrient seen in every run. Substantiation of the phase diagram and crystal growth feasibility (by spontaneous nucleation) were established during the run.

Our next run, (La-5), was an attempt to utilize a hot pressed mixture of La_2O_3 and Al_2O_3 as nutrient. Since spontaneous nucleation had been achieved in No. La-4, the same conditions were selected for La-5. The nutrient was in the form of a cylindrical brickette approximately 2 inches in diameter by 2 inches high. Crushing the brickette produced pieces of a size suitable for use as nutrient.

Hydrothermal Effort (continued)

If the particle size of the nutrient is too small, the physical appearance of a mixture of solvent and powder is that of a thick phase. The paste-like condition severely restricts solvent flow through the bulk of the nutrient. Only a very shallow layer on the top surface of the nutrient is available for dissolution. Flow restriction can readily cause subsaturation of the solvent during warm-up. Seeds in contact with a subsaturated solvent will dissolve until they are gone or until the liquid is saturated.

The crushed ruby and powdered La_2O_3 normally used as nutrient could be termed a "paste". The hot pressed nutrient did not turn entirely to paste during the run which is somewhat encouraging. However, the seeds still did not dissolve away completely. Further experiments will be conducted with sintered and/or hot pressed mixed powders and hydrothermally reacted $LaAlO_3$.

Two runs, Nos. La-6 and La-8 (La-7 deferred to future), were made at 1 m K_2CO_3 to test growth feasibility at the low molality end of the phase diagram. In both runs, the nutrient was reacted but no spontaneous nucleation was observed.

A tabular summary of the runs made to date is shown in Table IV.

D. Discussion

The phase stability study made to this time has not encompassed the full range of all variables. The data have been restricted to the pressure, solvent concentration and temperature conditions where it appeared

TABLE IV

Run No.	Date	Pressure	Growth Temperature	Dissolution Temperature	K_2CO_3 Molality	Remarks
La-1	5-5	9 K	475°C	528°C	7	No growth. Nutrient reacted to form $LaAlO_3$.
La-2	5-13	----	-----	-----	-	Leaked.
La-3	5-17	15 K	405°C	468°C	7	Seed dissolved, S. N. $La(OH)_3$.
La-4	6-1	11 K	438°C	495°C	7	Seed dissolved, S. N. $LaAlO_3$.
La-5	6-10	11.7 K	440°C	490°C	7	Seeds etched back, no growth, nutrient hot pressed mixture of oxides.
La-6	6-21	10.2 K	336°C	412°C	1	No. S. N., nutrient reacted, liquid milky.
La-7	Deferred to Future					
La-8	6-28	18.8 K	414°C	500°C	1	Seeds etched back, No. S.N., nutrient reacted, liquid milky.

S. N. - Spontaneous nucleation of $LaAlO_3$ crystals in growth chamber.

Hydrothermal Effort (continued)

to be desirable to carry out crystal growth, particularly below 435°C. From the data collected for the stability of $LaAlO_3$ and $La(OH)_3$, it was concluded that at 400°C crystallization of only $LaAlO_3$ could be carried out at reasonable pressures but only at very low (less than 2 m) or very high (greater than 7 m) K_2CO_3 concentrations.

Growth under other conditions would set up a transitory state in which $La(OH)_3$ would form until steady state conditions were attained. The existence of a high pressure form of $La(OH)_3$ had been shown by Shafer and Roy[6] who also reported the X-ray diffraction data for this phase. The phase diagram as reported by them is shown in Figure 8. The pressure and temperature conditions data for the appearance of this phase are in that area where crystal growth of $LaAlO_3$ would seem to be most desirable. Furthermore, the correspondence of these data with the findings of this study are in fair accord. Four small capsules were charged with La_2O_3, 7 m K_2CO_3 solution and then at 400°C subjected to pressures of 5,000, 10,000, 15,000, or 20,000 psi to check on the pressure solvent concentration dependency for the appearance of the high pressure $La(OH)_3$ phase. In all cases, part of the La_2O_3 was converted to $La(OH)_3$; the rate of conversion appearing to be pressure dependent. The greatest degree of conversion to $La(OH)_3$ occurred in the capsule operated at the highest temperature. The results of this experiment would indicate that the requisite pressure for the conversion to $La(OH)_3$ is lowered by the presence of base.

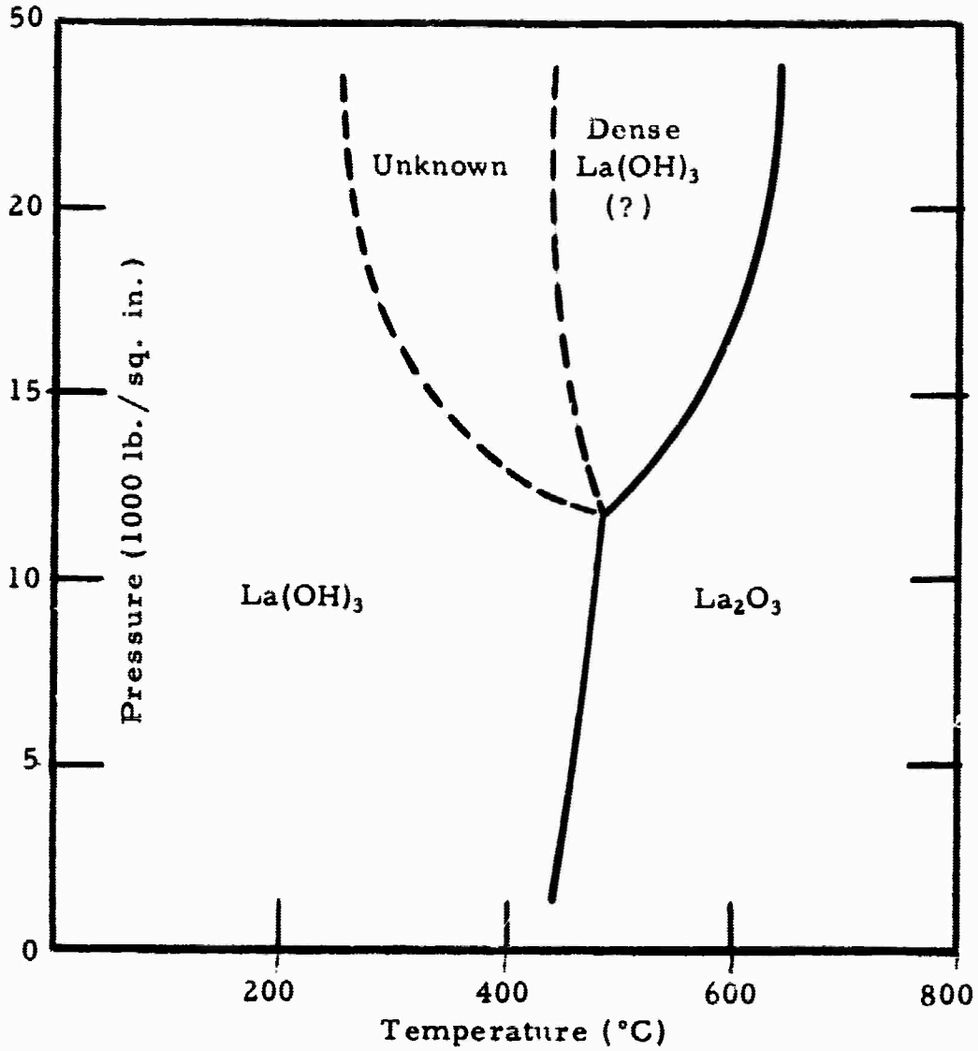

Figure 8

La_2O_3-H_2O Phase Diagram According to Shafer and Roy[6]

Hydrothermal Effort (continued)

The source and form of nutrient was shown to be somewhat of a problem in two ways. First, in attempts to prepare a sintered material, it was found that these samples would disintegrate on standing in air due to the hydroscopic nature of La_2O_3. This disintegration occurred even after firing the equimolar Al_2O_3-La_2O_3 mixtures to 2000°C. The high temperature vacuum pressed sample was fairly successful but further investigation of this material is required.

The second area where a lack of suitable nutrient produces difficulty is in calculation of the proper percent of fill necessary to produce a requisite pressure and temperature. The estimation of fill requires several runs in any case but we encountered more difficulty than anticipated. We believe this was due in part to the hydrolysis of La_2O_3 by the K_2CO_3 solutions changing the effective void volume when powdered La_2O_3 and crushed ruby were used.

Although extensive crystal growth on the seeds has not been obtained as yet, the observation of spontaneously nucleated crystals is most encouraging. The work for the coming months will be directed entirely toward the growth of large crystals.

VI. SUMMARY AND CONCLUSIONS

Precipitation of insoluble LaF_3 from PbF_2 melts render this solvent impractical for crystal growth of $LaAlO_3$ below about 1500°C soak temperatures and these high temperatures lead to rapid furnace and crucible failure. Of the solvent systems investigated, Bi_2O_3-B_2O_3 appears to hold the most promise as a substitute.

The phase stability and solubility studies of $LaAlO_3$ would indicate that solvent concentrations of less than 2 m or greater than 7 m K_2CO_3 should be used in order to grow crystals below the 435°C transition temperature for $LaAlO_3$. Seven runs have been made in the large autoclaves and, as anticipated, some difficulties have been encountered with nutrient and fill conditions. Spontaneous nucleation of $LaAlO_3$ in the growth chamber was achieved.

VII. PROGRAM FOR THE NEXT PERIOD

During the next period, we will:

1. Further attempts will be made to grow $LaAlO_3$ from $BaO-B_2O_3$.

2. Optimize growth conditions for the growth of $LaAlO_3$ in $Bi_2O_3-B_2O_3$ fluxes.

3. Use both the flux melt and sealed tube technique to determine solubility of $LaAlO_3$ in this system.

4. Grow crystals of $LaAlO_3$ at least 1 cm^2 of a quality suitable for use as hydrothermal seeds by slowly cooling large batches in the 6 inch furnace.

5. Continue to investigate possible nutrient sources.

   a. Sinter hydrothermally synthesized $LaAlO_3$.

   b. Sinter equimolar evaporated samples of lanthanum and aluminum, nitrates or oxalates.

6. Make further adjustments of fill conditions as required by nutrient changes.

7. Grow crystals in regions determined from phase study below 435°C.

8. Carry out an investigation of growth above 435°C.

9. Study the optical fluorescence of chromium doped samples as grown.

10. Determine dopant levels by X-ray analysis.

Program for the Next Period (continued)

11. Investigate quality of sufficiently large crystals for strains, dislocations, etc., by the Lang X-ray technique.

12. Investigate $LaAlO_3$ phase transition and relation to growth conditions.

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