ARPA Order No. 306-62
Project Code No. 4730

SEMIANNUAL TECHNICAL SUMMARY REPORT

FOR

HYDROTHERMAL GROWTH OF CRYSTALS OF $LaAlO_3$

15 August 1964 to 31 December 1964
NONR-4616(00)

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

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OFFICE OF NAVAL RESEARCH
NONR-4616(00)
ADVANCED RESEARCH PROJECTS AGENCY
ARPA 306-62

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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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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 will be examined such as regions of congruent solubility, crystal stability, and degree of solubility.

II. ABSTRACT

$LaAlO_3$ has been successfully grown in a hydrothermal system below and above the transition temperature of 435°C. Using small autoclaves, growth has been observed in the temperature range of 400°C - 600°C in 7 m K_2CO_3 at 10,000 to 20,000 psi. A high pressure form of $La(OH)_3$ is also stable within this temperature and pressure range.

Seed crystals up to 1/4 inches x 1/4 inches x 1/8 inches were grown from PbF_2 fluxes. These crystals are readily doped with Cr by the addition of Cr_2O_3 to the melt.

III. STATUS

This report covers only the four and one-half month period, August 15, 1964, to December 31, 1964. During this period of time, all the objectives established in the Milestone Chart at the start of the Contract for completion at this time have been met. Table I shows the original estimated completion dates and the present status of these objectives.

TABLE I

STATUS

Item	Goal	Purpose	Current Status	Problems Encountered or Expected	Original Estimated Completion Date	New Estimated Completion Date
1	Equipment preparation and material procurement	Provide equipment and materials for crystal growth experiments	Complete	None	9-65	----
2	Study to determine hydrothermal solvent suitable for $LaAlO_3$ recrystallisation below 435°C	Growth of $LaAlO_3$ below 435°C	Complete	None	10-65	----
3	Study to determine flux from which seed crystals can be grown	Solvent selection	Complete	None	11-65	----
4	Determine solubility of $LaAlO_3$ in hydrothermal solvent	Solubility curve	Changed to phase diagram determination	Stable $La(OH)_3$ phase found	1-65	4-65
5	Determine solubility of $LaAlO_3$ in molten salt solvent	Solubility curve	In progress	Stable LaF_3 phase found	2-65	4-65
6	Optimize growth conditions for large, high quality molten salt seed crystals	Provide large seed crystals	In progress	Stable LaF_3 phase formed by reaction of La_2O_3 with PbF_2. Non-liquid melt below 1200°C	3-65	3-65
7	Determine effect of temperature, pressure and ΔT on hydrothermal growth of $LaAlO_3$ crystals	Growth of large hydrothermal crystals	Not started	Waiting for shipment of large autoclaves	4-65	5-65
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	6-65	6-65
9	Grow large $LaAlO_3$ crystals hydrothermally	Contract objective	Not started	None	8-65	8-65
10	Evaluate $LaAlO_3$ crystals for Cr lifetime	Lifetime measurement	Not started	None	8-65	9-65
11	Write Final Report	Contract requirement	Not started	None	8-65	9-65

IV. EXPERIMENTAL

1. Introduction

Four possible techniques could be used to grow single crystals of $LaAlO_3$: flame fusion, melt, molten salt and hydrothermal. The flame fusion technique has been found capable of producing small crystals of $LaAlO_3$.[1] However, the problems associated with using this technique to produce laser quality ruby are more difficult for $LaAlO_3$ because of its stoichiometric requirements. Problems connected with equipment and materials that are encountered in attempting to grow from the melt are quite formidable. In addition to the high melting point of $LaAlO_3$, the solid-solid transition it undergoes at 435°C makes growth of sound crystals extremely difficult by any melt technique.

We have elected to use the two remaining techniques; namely, molten salt growth and hydrothermal growth. Crystals produced from a molten salt will be used as seed crystals in a hydrothermal growth program. The molten salt process, while capable of producing small crystals, would undoubtedly be non-competitive in really large crystal growth attempts with respect to hydrothermal techniques because of the cost of large crucibles and equipment that would be required. Not only does the hydrothermal technique lend itself to production of large crystals, but it is also theoretically capable of producing crystals which are of high quality and uniformity, and which exhibit low strain. In addition, one of the major problems in growing $LaAlO_3$, the phase transition at 435°C which all crystals grown at high temperatures must pass through, is eliminated because the hydrothermal technique has been used to grow crystals of quartz, ruby and zinc oxide below this temperature.

Our work, therefore, is planned around these two techniques: molten salt for seed crystals and possibly nutrient material, hydrothermal for growth of large crystals.

2. Molten Salt System

A. Experimental Method

1. Equipment

The molten salt method of crystal growth is a process whereby a crystal growing composition is heated above its liquidus temperature, and then slowly cooled to produce supersaturation. The process is usually carried out in platinum crucibles with a temperature difference (ΔT) established between the top and the bottom of the can, the bottom maintained cooler when solvent density exceeds solute density. The solvent is physically mixed with the solute in a proportion determined experimentally and placed in the platinum can which is then placed in the furnace. The furnace is held at a constant temperature long enough to dissolve the solute, after which the temperature is slowly lowered by a suitable programmer-controller to a preset temperature. The ΔT established between the top and bottom of the crucible with the bottom cooler than the top causes the crystals to nucleate at or near the bottom of the crucible where they are less subject to temperature fluctuations than they would be on the surface of the melt. The can is then withdrawn,

Experimental (continued)

the molten salt is poured off, and the single crystal yield is washed, usually in an acid to remove residual solvent.

The tube furnaces and associated equipment used in the molten salt growth of $LaAlO_3$ have been described in detail previously.[2] An improved system was built by R & D Product Co., see Figure 1. In order to achieve a rapid, hydraulic-like action, a system consisting of counter-balances and ball bearings were incorporated into the design. The pedestal platform is supported at four points by means of a micropitch chain terminating at four adjustable studs which enables the operator to tilt the pedestal in any direction, thus insuring an axis similar to that of the muffle tube. The desirable axis is guaranteed over the full range of travel by two parallel guide bars. A smooth rotation of the pedestal turntable was achieved by means of two special castings, one of which is extremely heavy. This casting is mounted on a sealed double thrust Timkin ball bearing. The packing seal of the bearing was removed and the manufacturer's grease was replaced with high temperature silicon grease.

Lateral movement of the pedestal is achieved by means of an oversized mounting of the turntable in the plate permitting lateral adjustments in all directions.

Operation of both the elevator and turntable are very much improved over the system described previously[2] and appear to offer trouble-free performance over the long term.

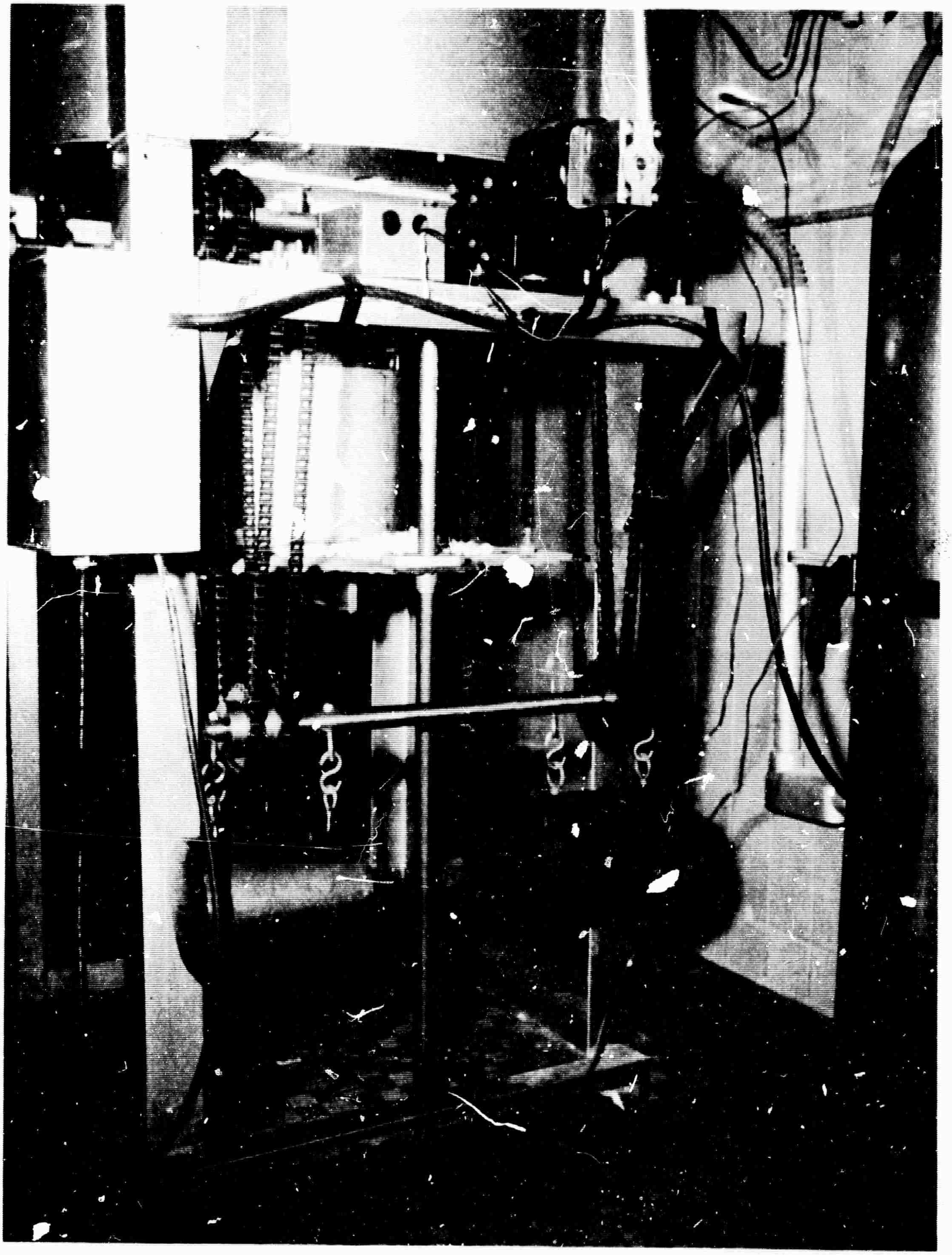

Figure 1
Improved Elevator Mechanism

Experimental (continued)

Other improvements incorporated in the design of the 6 inch furnace are:

1. An improved pedestal which consists of a removable top. Since most pedestal failure has resulted in the past from cracking or spillage of solvents on the upper one-fourth of the pedestal, it is hoped that this portion can now be replaced without having to discard the entire unit.

2. A plate, similar to that designed for the 10 inch furnace, upon which the crucible rests. This plate has a hole in the middle through which a thermocouple tube fits, enabling good centering of the platinum can as well as better temperature sensitivity of the thermocouple

In addition, the tongs used to lift the hot platinum crucible from the pedestal after the run is complete, can now fit under the crucible giving much better safety from possible slippage of the crucible and releasing pressure on the crucible walls. This is particularly important for 1200°C pours where the platinum crucible is quite soft.

3. Larger diameter heating elements (1 1/4 inch diameter) which because of their lower resistance and larger radiating surface area will last much longer than the previous 3/4 inch diameter rods. We have on order 1 1/3 inch Morganite spiral heating elements. These elements are the same make and diameter as the ones we have used so successfully for high temperature operations in the 10 inch furnace.

2. Solvent Selection

In work performed prior to the Contract, crystals of $LaAlO_3$ doped with Cr were grown in 250 ml platinum crucibles from 100 percent PbO duplicating the work of Remeika.[3] These crystals were small, averaging only about 1 mm^3, and in every case the platinum crucible in which the crystals grew had to be discarded because of extensive corrosion of the platinum. A 5 X scale-up using a 5 inch platinum can did not appreciably increase crystal size but did increase the corrosion rate resulting in premature failure of the can within the cool-down period. A search for another flux was immediately launched.

3. Phase Equilibria - Solubility

Solubility in molten salt systems can best be measured by heating the solvent and solute to a specified temperature long enough to insure complete solution, then lowering the temperature past the crystallization point until the pre-selected quench temperature is reached. At this point, the flux is poured into a water cooled platinum crucible and on cooling is analyzed for solute by wet chemical analysis. A series of these experiments yields a solubility curve. This method insures that the melt is saturated at the quench temperature, and reversibility is easily demonstrated.

B. Results

A summary of all molten salt runs is shown in Table II. Run No. 10 was used to test $PbF_2 + B_2O_3$ as a substitute for PbO. 22 m percent

TABLE II

MOLTEN SALT RUNS

Run No.	Units	La_2O_3	Al_2O_3	Cr_2O_3	PbF_2	B_2O_3	Totals	Purpose of Run	Furnace Used	Crucible Used	Soak Temp. (°C) Ped.	Soak Time (hrs)	Cooling Rate (°C/hr)	Pour Temp. Ped. (°C)	Remarks
10	gms	195.6	61.2	0.00	333.0	11.0	600.8	$LaAlO_3$ in PbF_2-B_2O_3	3"	250 ml	1300	1	100	1000	Incomplete solution.
	moles	0.600	0.600	0.00	1.358	0.158	2.716								
	m %	22.09	22.09	0.00	50.00	5.82	99.98								
11	gms	130.4	61.2	0.00	333.0	11.0	535.6	50% excess Al_2O_3	3"	250 ml	1300	1	100	1000	No pour, many small high quality crystals. Apparent excess of Al_2O_3.
	moles	0.400	0.600	0.00	1.358	0.158	2.516								
	m %	15.89	23.85	0.00	53.97	6.28	99.99								
12	gms	130.4	40.8	0.00	333.0	11.0	515.2	% yield at 1000°C	3"	250 ml	1300	1	100	----	Spilled.
	moles	0.400	0.400	0.00	1.358	0.158	2.316								
	m %	17.27	17.27	0.00	58.64	6.82	100.00								
13	gms	130.4	40.8	0.00	333.0	11.0	515.2	% yield at 1200°C	3"	250 ml	1300	1	100	1200	Controller broke. Many small crystals.
	moles	0.400	0.400	0.00	1.358	0.158	2.316								
	m %	17.27	17.27	0.00	58.64	6.82	100.00								
14	gms	195.6	61.2	0.00	333.0	11.0	600.8	Effect of slow cooling	3"	250 ml	1300	1	2	1000	Large good quality crystal growth.
	moles	0.600	0.600	0.00	1.358	0.158	2.716								
	m %	22.09	22.09	0.00	50.00	5.817	99.98								
15	gms	195.6	61.2	0.00	333.0	22.0	611.8	Effect of large B_2O_3 content in flux	3"	250 ml	1300	1	100	1000	Top pushed off and contents blown out. Heat more slowly.
	moles	0.600	0.600	0.00	1.358	0.316	2.874								
	m %	20.88	20.88	0.00	47.25	11.00	100.01								
16	gms	195.6	61.2	0.00	333.0	11.0	600.8	$LaAlO_3$ in PbF_2-B_2O_3	3"	250 ml	1300	1	100	----	Top pushed off and contents blown out. Heat more slowly
	moles	0.600	0.600	0.00	1.358	0.158	2.316								
	m %	22.09	22.09	0.00	50.00	5.817	99.98								
17	gms	130.4	40.8	0.00	333.0	11.0	515.2	Repeat of No. 12	3"	250 ml	1300	20	100	1000	Crystal growth but large co-precipitation of LaF_3 made separation impossible.
	moles	0.400	0.400	0.00	1.358	0.158	2.316								
	m %	17.27	17.27	0.00	58.64	6.82	100.00								
18	gms	176.0	55.1	0.00	299.7	9.9	540.7	Repeat of No. 10 and No. 16	3"	250 ml	1300	1	100	1000	Good crystal growth.
	moles	0.540	0.540	0.00	1.222	0.142	2.444								
	m %	22.09	22.09	0.00	50.00	5.817	99.98								
19	gms	156.5	49.0	0.00	266.4	17.6	489.5	Effect of large B_2O_3 content in flux	3"	250 ml	1300	1	100	----	Cover blew off.
	moles	0.480	0.480	0.00	1.086	0.253	2.299								
	m %	20.88	20.88	0.00	47.24	11.00	100.00								
20	gms	195.6	61.2	0.00	0.00	0.00	256.8	Fusion of La_2O_3 and Al_2O_3	3"	250 ml	1300	16	---	----	Fused but crumbled and fell apart later.
	moles	0.600	0.600	0.00	0.00	0.00	1.2								
	m %	50.00	50.00	0.00	0.00	0.00	100.00								
21	gms	195.6	61.2	1.3	0.00	0.00	258.1	Fusion of La_2O_3, Al_2O_3, and Cr_2O_3	3"	250 ml	1300	16	---	----	Mixed and ball milled but still not good fusion.
	moles	0.600	0.600	0.008	0.00	0.00	1.208								
	m %	49.67	49.67	0.66	0.00	0.00	100.00								
22	gms	176.0	55.1	0.3	299.7	9.9	541.0	Effect of high ΔT on growth of Cr doped $LaAlO_3$	3"	250 ml	1300	1	100	1000	Incomplete solution.
	moles	0.540	0.540	0.002	1.222	0.142	2.446								
	m %	22.09	22.09	0.04	49.96	5.81	99.99								
23	gms	158.4	49.6	0.3	269.7	8.9	486.9	Growth of Cr doped $LaAlO_3$	3"	250 ml	1300	1	2	1000	Cr doped $LaAlO_3$ not good quality.
	moles	0.486	0.486	0.002	1.100	0.128	2.202								
	m %	22.07	22.07	0.009	49.95	5.81	100.00								
24	gms	19.6	6.1	0.03	33.3	1.1	60.13	Effect of insulated crucible on crystal growth	3"	100 ml	1275	1	4	1000	Inconclusive. Quality of crystals about the same as in uninsulated 250 ml crucible.
	moles	0.060	0.060	0.0002	0.136	0.016	0.2722								
	m %	22.04	22.04	0.0007	49.96	5.88	99.98								
25	gms	158.4	49.6	0.3	269.7	8.9	486.9	Repeat of No. 22	3"	250 ml	1300	1	100	1000	Deep red $LaAlO_3$ crystals.
	moles	0.486	0.486	0.002	1.100	0.128	2.202								
	m %	22.07	22.07	0.009	49.95	5.81	100.00								
26	gms	158.4	49.6	0.03	269.7	8.9	486.63	Cr doped $LaAlO_3$	3"	250 ml	1340	2	2	950	Contents spilled.
	moles	0.486	0.486	0.0002	1.100	0.128	2.2002								
	m %	22.07	22.07	0.0007	49.95	5.81	100.00								
27	gms	158.4	49.6	0.03	269.7	8.9	486.63	Cr doped $LaAlO_3$	3"	250 ml	1300	1	10	1000	Good crystal growth.
	moles	0.486	0.486	0.0002	1.100	0.128	2.2002								
	m %	22.07	22.07	0.0007	49.95	5.81	100.00								
28	gms	158.4	49.6	0.00	269.7	0.00	477.7	Solubility determination	3"	250 ml	1300	64	30	1270	[illegible] our.
1-3	moles	0.486	0.486	0.00	1.100	0.00	2.072					1	30	1270	No pour.
	m %	23.46	23.46	0.00	53.09	0.00	100.01					1	10	1000	No pour.
29	.... Not Run														
30	.... Not Run														
31	gms	79.2	25.0	0.00	134.0	135.0	373.2	Solubi. determ. ation	3"	250 ml	1300	1	100	1200	Slight pour.
	moles	0.243	0.243	0.00	0.546	0.605	1.637								
	m %	14.84	14.84	0.00	33.35	36.96	99.99								
32	.... Not Run														
33	gms	71.3	22.5	0.00	122.6	116.1	332.5	Crystal growth	3"	250 ml	1300	2	12.5	1000	No pour, small crystals, good quality.
	moles	0.219	0.219	0.00	0.500	0.520	1.458								
	m %	15.02	15.02	0.00	34.29	35.67	100.00								

Experimental (continued)

La_2O_3 and an equimolar quantity of Al_2O_3 were dissolved in 50 m percent PbF_2 and 5.82 m percent B_2O_3. We did not know what concentration to use but we assumed the solubility of $LaAlO_3$ in PbF_2 was probably higher than in the PbO. A one hour soak was followed by a 100°C cool down. However, all the La_2O_3 and Al_2O_3 were not dissolved when cooling began and very small imperfect crystals were formed. Complete solution was obtained in Run No. 14 when identical conditions to No. 10 were used but a much slower cooling rate of 2°C per hour was used. This run produced large crystals up to 1/2 square inches on the surface of the melt, see Figure 2. The melt had solidified at the pour temperature of 1000°C. When the flux was dissolved in HNO_3, the crystals were found to be badly included plates which often broke into smaller fragments. Cr was incorporated into $LaAlO_3$ by the addition in Run No. 23 of 0.009 m percent Cr_2O_3 and in No. 26 and 27 of 0.0007 m percent Cr_2O_3.

In an attempt to achieve a pour of the melt after the run and to determine the yield of $LaAlO_3$ at different temperatures, two runs, No. 12 and 13, were made. In both runs, 17.27 m percent La_2O_3 and Al_2O_3 were added to 58.64 m percent PbF_2 + 6.82 m percent B_2O_3. No. 12 failed prematurely when the crucible tipped over during stirring but the other, No. 13, when cooled to 1000°C, was just as solid as all previous ones with the higher concentration.

Attempts to obtain solubility data in Run No. 28 (1-3), using 23.46 m percent La_2O_3 + Al_2O_3 in 53.09 PbF_2 and using 14.84 m percent La_2O_3

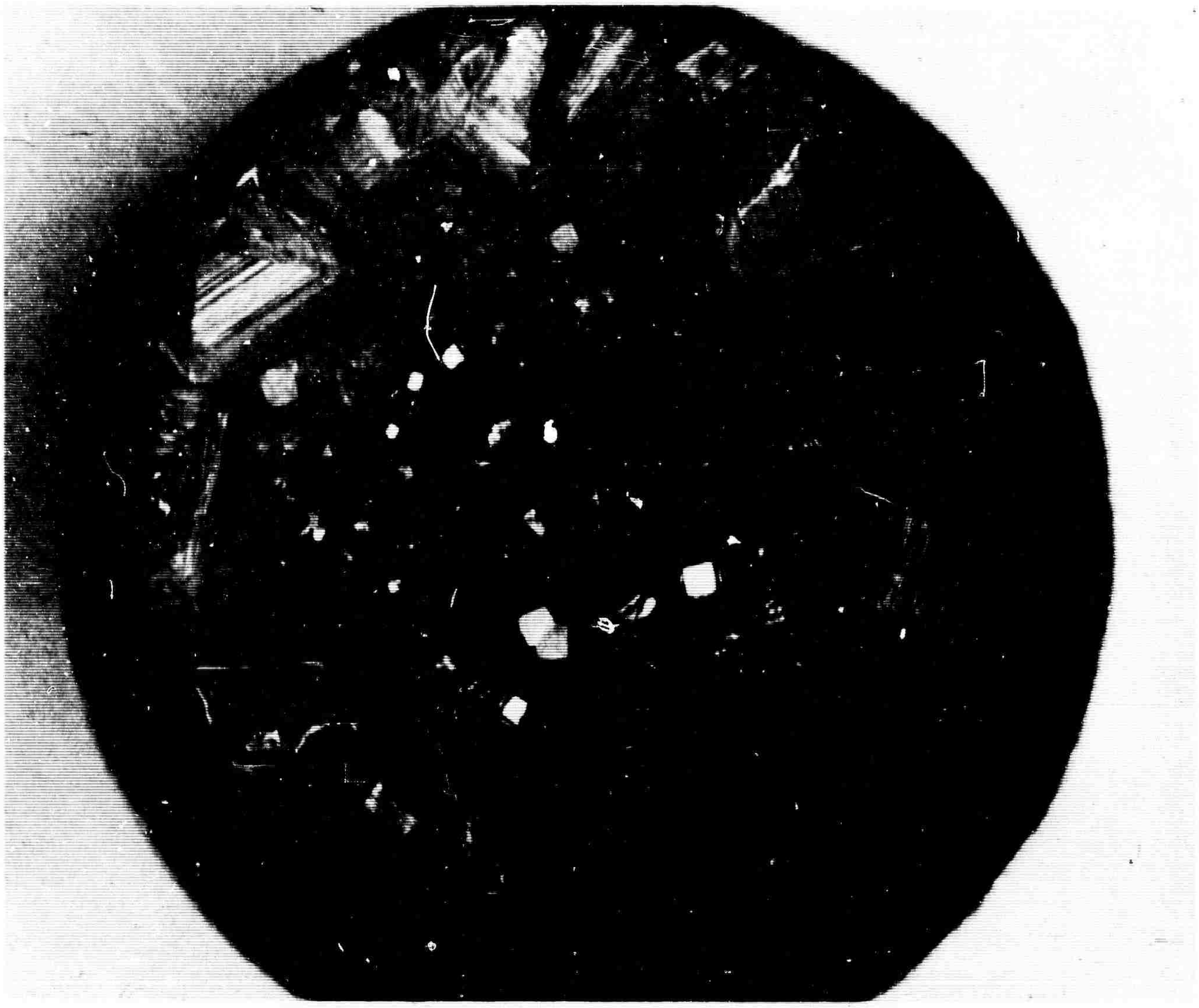

Figure 2

Large $LaAlO_3$ Crystals Grown from Molten Salt

Experimental (continued)

+ Al_2O_3 in 33.35 PbF_2 + 36.96 PbO were unsuccessful due to our inability to achieve a liquid melt even at high temperatures. Subsequent attempts will be made using much more dilute solutions.

Two attempts at achieving a sintering of La_2O_3 and Al_2O_3 (No. 20 and 21) for use in the hydrothermal system by firing equimolar mixtures at 1400°C were unsuccessful. The mixture then fell apart on standing probably due to the hydroscopic nature of the La_2O_3.

C. Discussion

We assumed that the difficulty in forming a single liquid phase resulted from precipitation of lanthanum tri-fluoride since the melt was not actually solid but appeared slushy. X-ray diffraction studies of the flux revealed that this was indeed the case. LaF_3 and $LaAlO_3$ were found in about equal quantities in the solidified flux. The addition of PbO helped only a little (No. 31 and 33) while larger additions of B_2O_3 caused a bubble of glass to form which pushed the cover of the crucible off and spilled PbF_2 inside the furnace.

The formation of LaF_3 probably occurs due to the reaction

$$La_2O_3 + 3\,PbF_2 \rightleftarrows 2\,LaF_3 \downarrow + 3\,PbO$$

Al_2O_3 probably reacts in a similar manner but AlF_3 is volatile.

$$Al_2O_3 + 3\,PbF_2 \rightleftarrows 2\,AlF_3 \uparrow + 3\,PbO$$

Therefore, the reaction

$$La_2O_3 + Al_2O_3 \rightleftarrows 2\,LaAlO_3$$

probably takes place in a flux which becomes increasingly rich in PbO. LaF_3 solubility probably decreases sharply from a PbF_2 rich flux to a PbO flux and it is likely that $LaAlO_3$ solubility varies also. It appears, therefore, that crystal growth of sound $LaAlO_3$ crystals is probably limited to the higher temperatures, perhaps above 1200°C, with crystal growth below this temperature restricted to extremely dilute solutions.

3. Hydrothermal System

A. Experimental Method

The hydrothermal method of crystal growth is a process by which an aqueous solution is held at a high temperature and pressure in order to dissolve a material (the nutrient) in one part of the system, transport it to another part of the system and there deposit it on a seed crystal. The process is carried out in sealed vessels called autoclaves with a temperature difference (ΔT) established between the top and bottom of the autoclave. The nutrient is normally placed in the lower hotter part of the autoclave and the seeds are mounted in the cooler upper part, see Figure 3. Transport of the hot solution from the region of the seeds is by convection. Once the solution reaches the seed region, it becomes supersaturated with respect to the seed material and deposits on the seeds. The cooler depleted solution then returns to the hotter zone by convection and dissolves more nutrient.

The hydrothermal technique thus permits variation in the pressure at which a crystal may be grown thereby allowing a variation in the growth

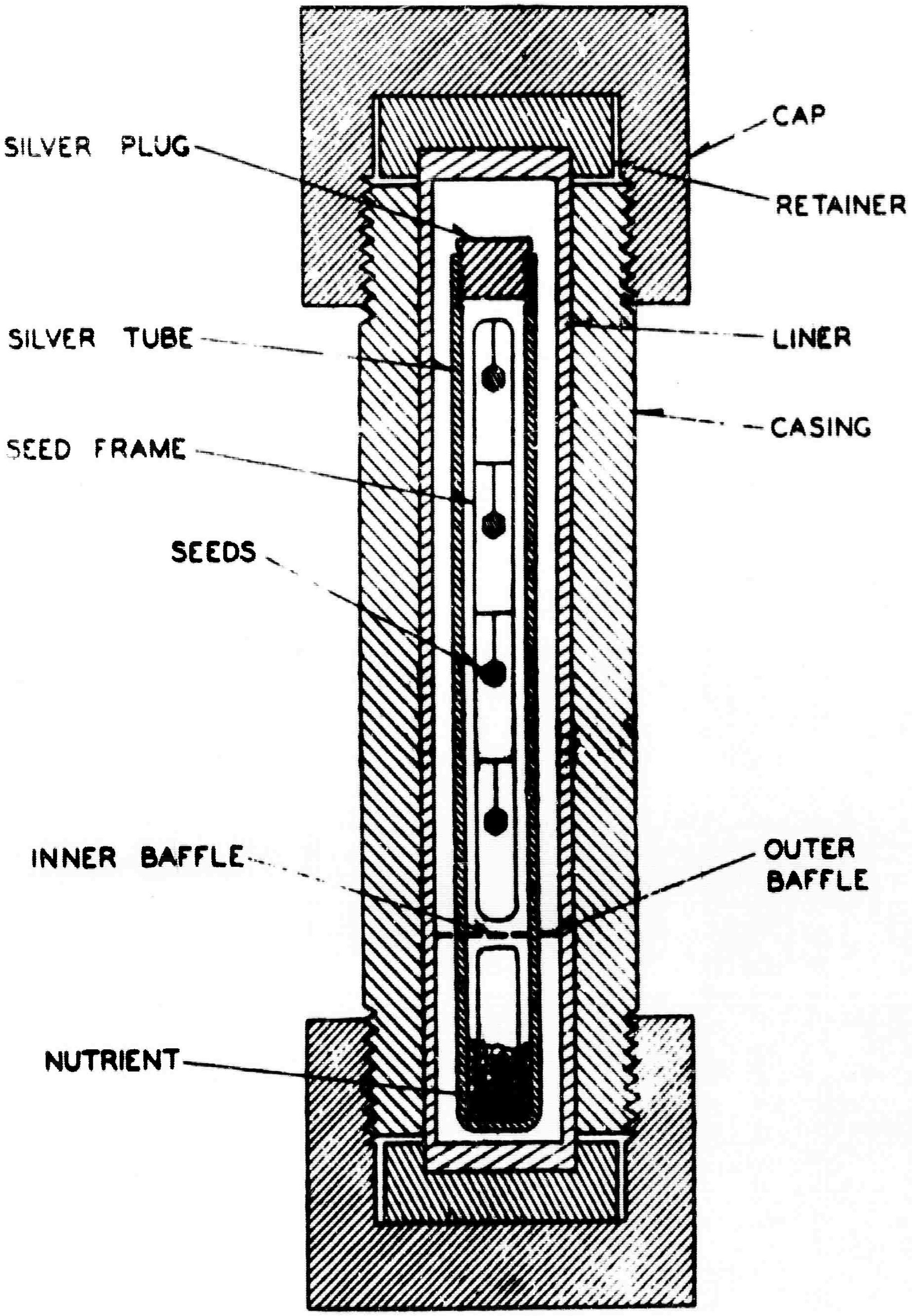

Figure 3

HYDROTHERMAL AUTOCLAVE

Experimental (continued)

temperature range, and the resulting changes in solubility and nucleation allow growth of large crystals which would be extremely difficult to grow any other way. The broad range of temperature and pressure also permits the growth from solution of crystals and crystal phases which would not be formed at atmospheric pressures.

Solvent selection is the first task associated with hydrothermal growth of new crystal. It is not sufficient, however, to demonstrate that a crystal has "dissolved" in a solution. Loss of weight of a crystal is often confused with "solubility" in an isothermal system when in reality the crystal has undergone an irreversible reaction, Also, in situ conversion and grain growth in an isothermal system can be extremely misleading. Therefore, the best system for solvent selection studies is not isothermal and workers at the Bell Telephone Laboratories and Airtron have devised a technique which is both rapid and efficient. It involves the use of small Stellite autoclaves in a set-up using four furnaces, a pressure pump, and valving system for applying pressure in controlled amounts. Such an apparatus is built and sold by the Tem-Pres Co. and is shown in Figure 4. This capsule is placed in the autoclave attached to the apparatus and inserted into a furnace. Usually four runs are made simultaneously.

Water is the pressure transmitting medium; the autoclave is heated and the desired pressure is achieved by release of water. The autoclave is positioned in the furnace so that there is a substantial temperature

Figure 4

Tem-Pres Apparatus

Experimental (continued)

difference between the bottom and the top of the vessel with the bottom being hotter.

The temperature gradient or ΔT is measured by means of two thermocouples inserted into wells on the outside of the autoclave but corresponding to the position of the seed and nutrient. The difference in temperature between these two positions is referred to as the "ΔT". After a period of time, usually 16 to 24 hours, the furnace is removed, the autoclave quenched, and the pressure released. The contents of the platinum capsule are examined. Promising solvents are those in which spontaneous nucleation or recrystallization on a seed has occurred at a point far from the original sample.

After a solvent has been selected, solubility is determined, but if the system is not simple; that is, if more than one phase is stable over the range studied, the phase diagram is determined at least for that portion of the system of immediate concern, after which growth conditions may be optimized.

Solubility is best determined by the weight loss method in which a crystal is held in a capsule in the presence of a known amount of solvent under the desired conditions of isothermal temperature and pressure until equilibrium is reached. The system is then quenched and the sample is removed, washed, dried, and weighed. Since the amount of solvent is known, the weight loss and the apparent solubility can be calculated. The composition of the solution, as well as temperature and pressure, are then varied to determine solubility curves.

Experimental (continued)

As in all crystal work, large systems are required to grow large crystals. Two large autoclaves have been ordered from Autoclave Engineers, Inc. They measure 28 3/4 inches long by 6 inches wide o.d. and 1 1/2 inches wide by 15 inches long internally. When these autoclaves arrive in March 1965, work will commence on growth of large, high quality hydrothermal $LaAlO_3$ crystals.

Since solvent selection is usually a major problem in achieving hydrothermal growth of a new crystal, it received our early attention. In the past, all but two of the large crystals grown hydrothermally have been grown from alkaline solutions. The most used solvents have been 1 - 5 molal NaOH, Na_2CO_3 or K_2CO_3. A surprising number of crystals have been grown from basic solutions. Examples are quartz, ruby, zinc oxide, calcium tungstate, and YIG. For this reason, alkali metal hydroxides and carbonates are the first solvents to use when trying to grow a new crystal.

B. Results

A summary of all hydrothermal crystal growth runs is shown in Table III. Attempts were made in Runs No. 1 - 12 to achieve recrystallization using 450 and 600°C at 20,000 and 30,000 psi in 7 m K_2CO_3, 7 m KOH, 1 m Na_2CO_3, and 7 m NaOH. Growth was first achieved in Run No. 13 using 7 m K_2CO_3 at 600°C and 20,000 psi. Growth of 136.17 percent was achieved in 77 hours, see Figure 5. Crystal dimensions were 0.240 inches by 0.282 inches by 0.150 inches. The nutrient consisted of 0.8617 grams of $LaAlO_3$ crystals grown from flux and 0.1370 grams of sapphire. Using similar con-

TABLE III

HYDROTHERMAL $LaAlO_3$ CRYSTAL GROWTH

Run No.	Nutrient Wt. Before	Nutrient Wt. After	Δ Wt. Nutrient	Wt. of Solvent Before	Seed Wt. + Wire Before	Seed Wt. + Wire After	Δ Wt. of Seed (gms)	% Δ Wt. of Seed (gms)	Solvent	Temp. (°C) Top	Temp. (°C) Bot.	ΔT (°C)	Dist. between T/C	Pres lbs/in²	Duration (hrs)	Remarks
1	0.7008	1.0106	+0.3098	2.5327	0.3232	0.2924	-0.0308	-------	7 m K_2CO_3	---	450	---	--	30,000	48	Some indication of growth but very slight.
2	1.1113	1.0928	-0.0185	2.2910	0.3838	0.3626	-0.0212	-------	7 m KOH	---	450	---	--	30,000	48	No growth.
3	0.9748	0.9730	-0.0018	1.8457	0.3218	0.3012	-0.0206	-------	1 m Na_2CO_3	---	450	- -	-	30,000	48	No growth
4	0.8830	0.8702	-0.0128	2.4190	0.3390	0.2758	-0.0632	-------	7 m NaOH	---	450	---	--	30,000	48	No growth.
5	0.7516	0.7382	-0.0134	1.9120	0.1950	0.1746	-0.0204	-------	1 m Na_2CO_3	---	450	---	--	30,000	96	No growth.
6	0.8806	0.5385	-0.3421	3.8212	0.2973	0.2683	-0.0290	-------	7 m K_2CO_3	---	600	---	--	20,000	54	100% fill, no growth.
7	0.9516	0.7738	-0.1778	2.6810	0.3192	0.2960	-0.0232	-------	7 m K_2CO_3	---	600	---	--	20 000	54	No growth.
8	1.0935	0.9467	-0.1468	2.8282	0.3136	0.2750	-0.0386	-- ----	7 m K_2CO_3	---	600	131	4"	20,000	54	No growth.
9	0.8672	0.6022	-0.2650	2.9934	0.2027	0.1852	-0.0175	-------	7 m K_2CO_3	---	600	---	--	20,000	54	Leaked, no growth.
10	0.7486	0.6421	-0.1065	2.7892	0.2841	0.1941	-0.0900	-------	7 m K_2CO_3	---	600	119	4"	20,000	48	No growth, Cr doped $LaAlO_3$ nutrient and undoped seed.
11	0.9498	0.7776	-0.1722	2.8727	0.2061	0.1882	-0.0179	-------	7 m K_2CO_3	---	600	---	--	20,000	48	No growth, Cr doped $LaAlO_3$ nutrient and undoped seed.
12	0.9289	0.7701	-0.1588	2.8799	0.2943	0.2634	-0.0309	-------	7 m K_2CO_3	---	600	---	--	20,000	48	No growth. Cr doped $LaAlO_3$ nutrient and undoped seed.
13	0.9987	0.3716	-0.6271	2.7706	0.3171	0.7489	+0.4318	+136.17	7 m K_2CO_3	--	600	---	--	20,000	77	Growth, undoped $LaAlO_3$ nutrient and sapphire.
14	0.6294	------	-------	2.6086	0.3872	0.8629	+0.4757	+122.86	7 m K_2CO_3	---	600	121	4"	19,900	66	Growth.
15	0.6028	0.3567	-0.2461	2.5705	0.2563	0.1893	-0.0670	-------	7 m K_2CO_3	---	600	---	--	20,500	66	No growth, leaked.
16	0.8769	0.6336	-0.2433	2.9676	0.2882	0.2686	-0.0192	-- ----	7 m K_2CO_3	413	464	51	3"	20,000	163	No growth.
17	0.8476	0.6743	-0.1733	2.9556	0.3547	0.2954	-0.0593	-------	7 m K_2CO_3	408	457	49	3"	20,000	163	No growth.
18	0.8035	0.2613	-0.6422	2.5240	0.1709	0.3808	+0.2099	+122.82	7 m K_2CO_3	421	510	89	3"	20,000	96	Growth, leaked.
19	0.8911	0.8915	+0.0004	2.8783	0.2504	0.1829	-0.0775	-------	7 m K_2CO_3	426	494	68	3"	22,000	163	No growth.
20	1.0171	1.0580	+0.0409	2.7989	0.1946	0.0645	-0.1301	-------	7 m K_2CO_3	419	473	54	3"	22,500	163	No growth.
21	1.0104	------	-------	2.9512	0.2711	0.9590	+0.6879	+253.74	7 m K_2CO_3	472	546	74	3"	20,000	163	Growth.
22	1.1923	0.9814	-0.2109	2.8060	0.3187	0.3235	+0.0048	+ 1.51	7 m K_2CO_3	426	487	61	3"	35,000	163	Slight growth.
23	0.9939	0.3150	-0.6789	2.9524	0.2875	------	-------	-------	7 m K_2CO_3	427	537	110	3"	25,000	163	No growth.
24	1.0994	0.6250	-0.4744	3.0079	0.2325	0.6284	+0.3959	+170.28	7 m K_2CO_3	417	492	75	3"	22,500	163	Growth.
25	1.1162	------	-------	2.8731	0.1352	0.2542	+0.1190	+ 88.02	7 m K_2CO_3	452	551	99	3"	21,000	112	Growth, only undoped material deposited on Cr doped seed.
26	1.0584	------	-------	2.8941	0.1180	0.1680	+0.0500	+ 42.37	7 m K_2CO_3	455	540	85	3"	21,000	112	Growth, only undoped material deposited on Cr doped seed.
27	1.1398	------	-------	2.9157	0.2243	0.1904	-0.0339	-------	7 m K_2CO_3	423	491	68	3"	21,000	144	No growth, non-doped seed, doped nutrient.
28	1.0635	------	-------	2.8342	0.2174	0.2057	-0.0117	-------	7 m K_2CO_3	433	500	67	3"	20,000	96	No growth, non-doped seed, doped nutrient.
29	1.0047	------	-------	2.8791	0.3278	0.3478	+0.0200	+ 6.10	7 m K_2CO_3	411	461	50	3"	10,000	112	Growth, no Cr deposited.
30	1.0189	------	-------	2.8622	0.2192	0.2507	+0.0315	+ 14.86	7 m K_2CO_3	411	478	67	3"	12,000	112	Growth, no Cr deposited.
31	1.0190	------	-------	2.8817	0.2152	0.2723	+0.0571	+ 26.53	7 m K_2CO_3	420	512	92	3"	15,000	112	Growth, no Cr deposited.

Figure 5

Hydrothermally Grown $LaAlO_3$

ditions, but no excess Al_2O_3, growth of 122.86 percent was achieved in 66 hours in Run No. 14.

Attempts were now made to produce growth below the 435°C transition temperature in K_2CO_3. Runs No. 16 through 18 were made with success in the case of No. 18. In this run 122.82 percent growth was achieved at 421°C and 20,000 psi with a ΔT of 89°C in 96 hours. Several other runs made in an attempt to duplicate this result was unsuccessful until Run No. 24 which produced 170.28 percent growth under conditions similar to Run No. 18. It was still not possible to obtain growth in every capsule in which these conditions existed. Table III shows that if Run No. 18 and 24 produced better than 100 percent increase in seed weight then Nos. 16, 17, 19, 20, 22, and 23 should have shown some weight increase also. The Tem-Pres apparatus achieves pressure by means of water as described previously. Pressure balance between the inner platinum capsule and the water is achieved by varying the percent fill. At low temperatures and high pressures, even a full capsule may fail to achieve sufficient internal pressure and will collapse partly at operating conditions. It was decided that perhaps the platinum capsule was being collapsed at 20,000 psi in different ways, which physically separated the seed from the systems, depending on small variations in percent fill, etc. It was decided to make three runs at lower pressures. Runs Nos. 29, 30, and 31 were made at 10,000, 12,000, and 15,000 psi, respectively. In each case, growth was achieved.

Experimental (continued)

Attempts were now made to grow Cr doped $LaAlO_3$ below 435°C. Seven runs, Nos. 25, 26, 27, 28, 29, 30, and 31, were made using Cr doped $LaAlO_3$ nutrient and doped or undoped seed crystals. In each case in which growth occurred, little or no Cr was deposited and growth rate appeared to be less than when Cr was absent. Similar results were observed in ruby hydrothermal growth.[4] In the case of ruby, changing the solvent concentration was found to be effective in alleviating this problem and a similar approach will be tried once the larger autoclaves are available.

In addition to $LaAlO_3$, spontaneously nucleated crystals of one or two additional crystalline forms were observed in all crystal growth runs. X-ray examination indicated that one form was spontaneously nucleated $LaAlO_3$ with a change in the external morphology from cube shaped crystals to slightly distorted dodecahedra, very similar in external appearance to flux grown YIG and YAG, see Figure 6 a and 6 b. The other was a second phase identified as a high pressure form of $La(OH)_3$.

The spontaneously nucleated dodecahedra of $LaAlO_3$ appeared in great profusion in the crystal growth runs below 425°C and mainly in the vicinity of the seed crystal. The quality of these crystals was very high. They were completely clear, with no evidence of cracking or veiling inclusions. Because this different habit of the crystals occurs only below 425°C, it may be possible that this nucleation is in some way related to the

Figure 6 a

Spontaneously Nucleated $LaAlO_3$

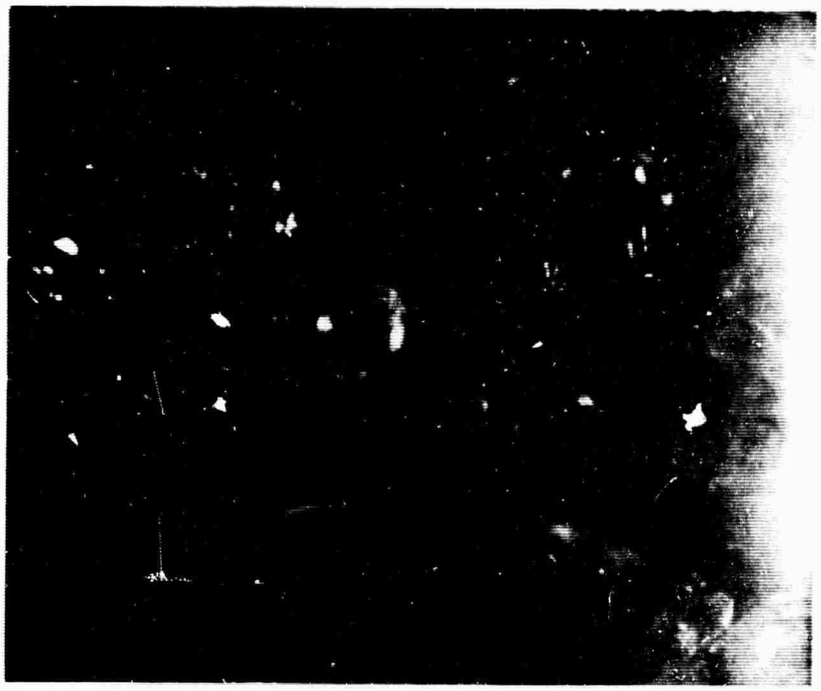

Figure 6 b

Spontaneously Nucleated $LaAlO_3$

phase transition. The quality of these crystals is sufficiently high to warrant attempts at the production of larger crystals in large autoclaves.

These crystals are at present very small measuring less than 1 mm^3. With the large autoclaves and longer runs, larger crystals should grow which can then be used as seeds for further growth.

A summary of the hydrothermal solubility determinations is shown in Table IV. All runs were made at 20,000 psi. The values varied widely mainly because of the formation of a high pressure form of $La(OH)_3$ at the temperature, pressure and solvent concentration range we selected. It is necessary, therefore, to determine that portion of the phase diagram in this range. This work is underway.

C. Discussion

It appears that a considerable amount of time, about 48 hours, is required for equilibrium to be achieved in this system. This is the reason for the two day delay before crystal growth is initiated. This period is apparently not sufficient for Cr equilibrium to be achieved since all crystal growth has been completely lacking in Cr. As indicated previously, this will be corrected by solvent concentration adjustments rather than additions of $K_2Cr_2O_7$ which in the case of ruby severely limited growth rates.

The appearance of $La(OH)_3$ indicates a rather limited stability range for $LaAlO_3$. With the relatively poor temperature controls available, as well as the heat-up and cool-down periods, it is possible that the $La(OH)_3$

TABLE IV

HYDROTHERMAL SOLUBILITY OF $LaAlO_3$ IN 7 m K_2CO_3

Run No.	Average Temp. (°C)	Duration (hrs)	Nutrient Before	Nutrient After	Δ Wt. Nutrient	Solvent Wt.	% Solubility
1	498	16	0.2375	0.2035	0.0340	0.8706	3.91
2	502	40	0.3100	0.2630	0.0470	0.8695	5.41
3	497	64	0.3116	0.2720	0.0396	0.8747	4.53
4	495	16	0.2570	0.2220	0.0350	0.8378	4.18
5	500	40	0.3336	0.2994	0.0342	0.9124	3.75
6	506	40	0.2643	0.2249	0.0394	0.9010	4.37
7	493	64	0.2445	0.1884	0.0561	0.8330	6.73
8	497	64	0.2510	0.2229	0.0281	0.8271	3.40
9	496	64	0.2683	0.2300	0.0383	0.8442	4.54
10	393	40	0.2622	0.2375	0.0247	0.8415	2.94
11	400	40	0.2807	0.2728	0.0079	0.8257	0.96
12	598	40	0.3015	0.2672	0.0343	0.8380	4.09

forms on passing through some temperature range. The appearance of the spontaneously nucleated $LaAlO_3$ dodecahedra, however, which appears only in those runs below 425°C and only in the vicinity of the seed crystal, would indicate stability under these conditions. It is felt that since the seed crystals are prepared at high temperatures from flux and are quenched at about 1000°C, we may be observing here a low temperature habit of $LaAlO_3$ never before seen.

V. SUMMARY AND CONCLUSIONS

1. Molten Salt System

Use of PbF_2 instead of PbO as a solvent has resulted in dramatic increase in $LaAlO_3$ size and a reduction in corrosion of the platinum container. However, the formation of LaF_3 and possibly volatile AlF_3 present further problems which must be solved before further progress can be made. The solubility of $LaAlO_3$ and LaF_3 in PbF_2 must be determined, and a better understanding of the mechanism involved must be found.

2. Hydrothermal

It has been demonstrated that single crystals of $LaAlO_3$ can be grown below 435°C at reasonable rates from K_2CO_3 at 10,000 to 20,000 psi. The stability of $La(OH)_3$ under some of these conditions means that the phase diagram of the system must be determined in this area. The profusion of spontaneously nucleated dodecahedra shaped $LaAlO_3$ of high optical quality is interesting because of the possibility that they are somehow related to a low temperature form of $LaAlO_3$.

VI. PROGRAM FOR THE NEXT PERIOD

1. Molten Salt Work

During the next period, we will determine the solubility curve of $LaAlO_3$ in PbF_2. We plan to proceed in the following way:

a. La_2O_3 and Al_2O_3 will be dissolved in PbF_2 in concentrations sufficiently dilute to insure at least a partial pour can be made at quench temperatures. Points will be established at 50°C intervals from 1350°C to 1000°C.

b. Samples of the pour will be given to X-ray for analysis of $LaAlO_3$, LaF_3, PbO, and PbF_2 by comparison with standards which have been prepared and to Mr. Townsend for wet chemical analysis.

c. A number of runs will be made in sealed cans and capsules to determine the effect, if any, that oxygen plays in the reaction and to establish reversibility of the reaction.

d. Attempts will be made to grow large, high quality seed crystals by premelting large batches and slow cooling in the 6 inch furnace.

2. Hydrothermal

a. The phase diagram in the 400°C - 600°C temperature range, the 10,000 to 20,000 psi range, and solvent concentrations from 1 to 7 molal K_2CO_3 will be determined by a series of experiments in the Tem-Pres.

b. As soon as the large autoclaves arrive, work will begin on the determination of ΔT, temperature, pressure, solvent concentration, and seed orientation on growth rates and crystal quality.

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