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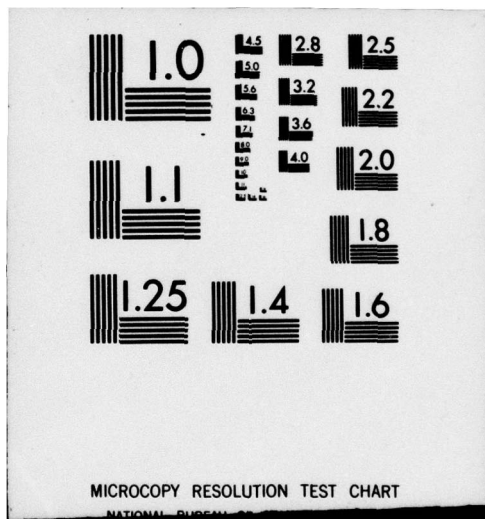
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<p>This report describes the preparation of both polycrystalline and single crystal host materials which may prove to be suitable for new lasers. Three classes of hosts were examined along with specified lanthanide dopants. The latter were most frequently the elements Ce, Pr, Er, and Yb. Single crystals of YAG were grown by the Czochralski method in production pullers. Dopants were added under controlled atmospheric conditions. Various</p>		

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fabricated optics such as polished rods, disks, or rectangular parallelepipeds were constructed for active laser testing. A significant study was made on high melting oxidic hosts with a fluorite crystal structure. Among these were stabilized ZrO_2 , CeO_2 , and ThO_2 . Sintered materials were prepared at $2000^\circ C$ in iridium crucibles. Single crystals were prepared by a "skull melting" or crucibleless method. The dopant Ce^{3+} was studied extensively by atmosphere control, charge compensation, and co-doping. Finally single crystals of KY_3F_{10} and YF_3 were grown by a Czochralski or top seeded solution method³ in an HF atmosphere. Dopants of Ce^{3+} and Pr^{3+} were added. All materials were tested for possible laser action, energy levels, fluorescence, and other spectral information at various contractor or academic laboratories.

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FOREWORD

This Annual Summary Report describes several related activities in materials preparation. The major portion is directly concerned with specific rare earth doped (Ce^{3+} or Pr^{3+}) polycrystalline or single crystal compounds which may prove to be suitable for possible d-f lasing schemes. Fluorite structured oxides such as ZrO_2 , CeO_2 , and ThO_2 were examined. Another portion of the effort was directed towards the growth, laser fabrication, and testing of doped YAG crystals. Finally, attempts to prepare $\text{YF}_3:\text{Pr}$ are described. The report summarizes all efforts under Contract No. N00014-76-C-0770 for the period October 1, 1977 to October 1, 1978. The contract work was under the coordination of Dr. Van O. Nicolai of the Office of Naval Research.

All compound preparation, single crystal growth, and laser rod fabrication were performed in the laboratories of Airtron Division of Litton Systems, Inc., 200 E. Hanover Avenue, Morris Plains, New Jersey 07950. Dr. Roger F. Belt was the technical director of the project and Dr. Larry Drafall was the project engineer. Dr. Robert Hartzell prepared all single crystal ZrO_2 compounds. Karl Jensen was the senior technician. Steven Turner performed all laser material fabrication and Joseph Latore provided all coated optics. Active testing of laser samples was conducted at Naval Research Laboratory by Dr. Leon Esterowitz or by Prof. William Yen of University of Wisconsin. The report was prepared by Roger F. Belt and Larry Drafall and released for publication in December 1978.

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1.0 INTRODUCTION

All of the present solid state crystal lasers are based on trivalent rare earth ions with weak forbidden $4f \rightarrow 4f$ transitions for optical emission and absorption. In recent years more attention has been given to alternate schemes for laser action which use very intense allowed interconfiguration $5d4f^{n-1} \rightarrow 4f^n$ transitions. These excited bands for most of the rare earth ions are at energies above 50000 cm^{-1} (6.2 eV). Therefore in some single crystals or glasses the fundamental band absorption of the host may prevent fluorescence from 5d bands. In other cases 5d excitation may be quenched by non-radiative decay to overlapping levels of the ground $4f^n$ configuration. However there are important exceptions. The energy level structure of an ion may be one where there are no 4f levels to quench 5d bands. This occurs in certain ions such as Ce^{3+} , Eu^{2+} , and Yb^{2+} .

Work in several laboratories has been directed towards examining spectra and designing materials which may give $5d \rightarrow 4f$ type lasing. This class of laser has several potential advantages. Among these are broad optical pump bands centered in the near uv, possible four level operation at 25°C , band emission in the visible, tunability over several hundred Å, and high quantum efficiency. Such a laser is a solid state analog of a dye laser. By appropriate choices of rare earth ion and host, oscillation wavelengths may be adjusted for specific applications in laser technology.

While the spectra, laser scheme, and possible materials have been studied in some systems, no working laser has been developed yet. The reasons for this are many but a greater understanding of allowed transitions of 4f impurity ion systems in crystalline environments is essential as a start. These studies include the crystal structure of the host, the effect of different coordination about the impurity ion, and symmetry principles. Some of the basic data can be collected from an examination of polycrystalline material but a single crystal is more helpful. Further simplification of emission and absorption in 5d→4f systems may be obtained by examining a system such as Ce^{3+} in $Y_3Al_5O_{12}$. This system was studied⁽¹⁾ and further hosts were reported later⁽²⁾. Some operating principles were determined but even for Ce^{3+} the spectra were not predictable and are very sensitive to structure.

Some recent measurements⁽³⁾ on the excited state absorption in $YAG:Ce^{3+}$ have been reported. Absorption bands due to 5d levels are found at the wavelength of its fluorescence. The resulting self absorption inhibits stimulated emission and is probably a loss mechanism. Whether this mechanism occurs in other hosts doped with Ce^{3+} is not known.

During the past few years we have studied many of the common oxide and fluoride hosts doped with Ce^{3+} . These have not been satisfactory because emission has been at an undesirable wavelength or the unactivated host has had intrinsic absorption in the excitation or emission region. Recent work has indicated

that Ce^{3+} in HfO_2 appears to give emission at a wavelength near 480mm. The crystal structure of HfO_2 and its homologs consists of a fluorite type (CaF_2) lattice where the metallic cations have eight equidistant neighbors at the corners of a cube and the anions have four equidistant neighbors at the corners of a regular tetrahedron. The fluorite type structure is restricted to compounds of the type RX_2 where R is a small cation and X is a larger anion. The anion is usually composed of O^{2-} , F^- , Cl^- , or OF^- in an ordered or random fashion and must be about 1.37 times the cation radius or a new structure (rutile, TiO_2) forms. Table I gives a list of the more common oxides and fluorides which crystallize with the fluorite lattice under special conditions. Note that most of these are radioactive and all oxides have melting points above $2600^\circ C$. This means a crucible material like iridium (m.p. of $2450^\circ C$) is not useful to contain a melt. The least complicated phase equilibria are found in the ZrO_2 , HfO_2 , and ThO_2 systems. The first two are quite similar because of their nearly identical cation radii and unit cell structures. The cubic fluorite structures of both ZrO_2 and HfO_2 can be stabilized at low temperatures by the addition of CaO , MgO , Y_2O_3 , and rare earths. The amount of stabilizing agent required is about 10-40 mole %. ThO_2 is unique in that it possesses a cubic phase without the addition of stabilizers.

The mode of incorporation of either a divalent or trivalent ion for Zr^{4+} in ZrO_2 suggests that the latter is oxygen deficient. This is also confirmed by the monoclinic structure of the ZrO_2 mineral baddeleyite which is composed of a seven coordinated Zr instead of eight. Another possibility is the presence of some type of vacancy ordered fluorite related structures. A few of these have been found for both CaO and Y_2O_3 stabilized products.

Table I
Compounds With Fluorite Structure

<u>Compound</u>	<u>Cation Radius (a) (A)</u>	<u>Estimated m.p. (°C)</u>	<u>Radioactive</u>
ZrO ₂	0.79	2800	no
HfO ₂	0.78	2780	no
ThO ₂	1.02	3300	yes
CeO ₂	0.94	2600	no
PrO ₂	0.92	?	no
NpO ₂	0.95	?	yes
PuO ₂	0.93	2300	yes
AmO ₂	0.92	?	yes
PoO ₂	?	?	yes
CmO ₂	?	?	yes
UO ₂	0.97	2850	yes
SrF ₂ (b)	1.12	1250	no
BaF ₂	1.34	1380	no
CaF ₂	0.99	1425	no

Notes: (a) Based on Ahrens tabulated values; the comparable value for Ce³⁺ is 1.07A.

(b) Not all fluorides and other halides are listed.

At high temperatures the O^{2-} are in a disordered state while at the lower temperature some anion ordering is prevalent with the development of a new structure. Small amounts of Ce do not radically change this situation. One asset may be the fact that in ZrO_2 , HfO_2 , or ThO_2 the favored valence state of substitution may be Ce^{3+} . This question can be answered only by preparation of compounds under controlled conditions. Atmospheres of H_2 , O_2 or other gases may also be effective to stabilize the possible $Ce^{4+}-Ce^{3+}$ equilibria. Under any circumstance the formation of a stabilized fluorite structure is required for a laser crystal since volume changes of other phases are usually disastrous for quality and integrity.

2.0 EXPERIMENTAL

The preparation of large single crystals of doped $Y_3Al_5O_{12}$ (YAG) was performed on Airtron's production type Czochralski growth stations. One of these is illustrated in Figure 1. Iridium crucibles of 2 or 3 inch diameter were used to contain the melt and to serve as a susceptor for the 450 KHz RF heating. The crucibles were contained within a glass bell jar in order to maintain a controlled atmosphere. A mixture of $N_2 - O_2$ was used for oxidizing conditions and one of $N_2 - H_2$ for reducing conditions. These atmospheres were used mainly for valence control in YAG:Ce. All crystals were doped with various rare earths in a range of 0.05 to 10%. Appropriate segregation coefficients were applied for each doping element. Total crystal lengths of 4-6 inches and a diameter of 1 inch were grown. Those boules were sufficient to provide up to a (1/4 x 3) inch laser rod plus additional pieces for sizeable polished rectangular blocks, cubes, or disks.

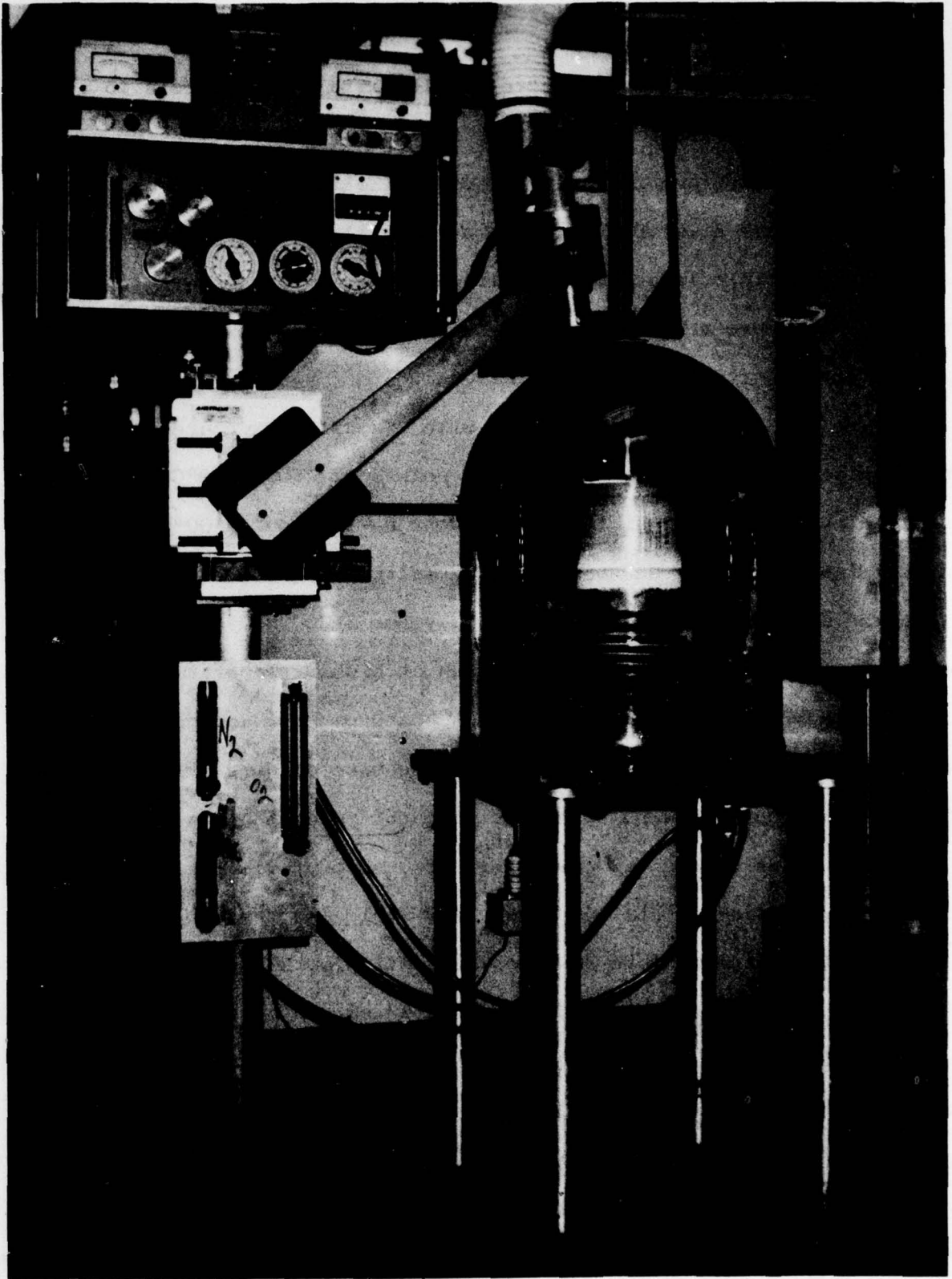


Figure 1. Czochralski Growth Station
for Doped YAG.

All samples were cut or core-drilled with diamond tools to rough shape. The polishing of each sample to laser specifications on orientation, flatness, perpendicularity, and parallelism of end faces, was performed in the Airtron manufacturing facilities. The AR coatings of single or multiple layers were applied at Lambda using production equipment. These were materials chosen to give less than 0.1% reflection loss at the chosen wavelengths of operation.

The preparation of the oxides with fluorite structure was a trying process because of their high melting points of 2600-2800°C. In low O₂ containing atmospheres sintering was done up to about 2300°C by means of an iridium crucible. However complete melting required some method other than the use of a crucible. Fortunately for ZrO₂, HfO₂, or ThO₂ the electrical conductivity is large enough at higher temperatures to act as a direct susceptor in MHz RF induction heating. Thus so-called "skull" or crucible-less methods have been used to make cm size single crystals. In this procedure the ZrO₂ was first brought to a high temperature of 1500°C by means of a metal powder or metal susceptor. As the temperature increases, a direct coupling between the field and the ZrO₂ is possible for additional temperature rise to the melting point. The molten ZrO₂ is held in a cooler surrounding powder shell which can be supported by itself or a metal water-cooled container. The main requirement of the skull method for melting ZrO₂ or HfO₂ was the 50-100 KW RF generator with a preferred operating frequency of 1-6 MHz. Associated coils, ceramic-ware, and control equipment were designed at a moderate cost. The apparatus at Airtron is pictured in Figure 2 where the ceramic construction and surround-coil are shown prepared for a trial run.

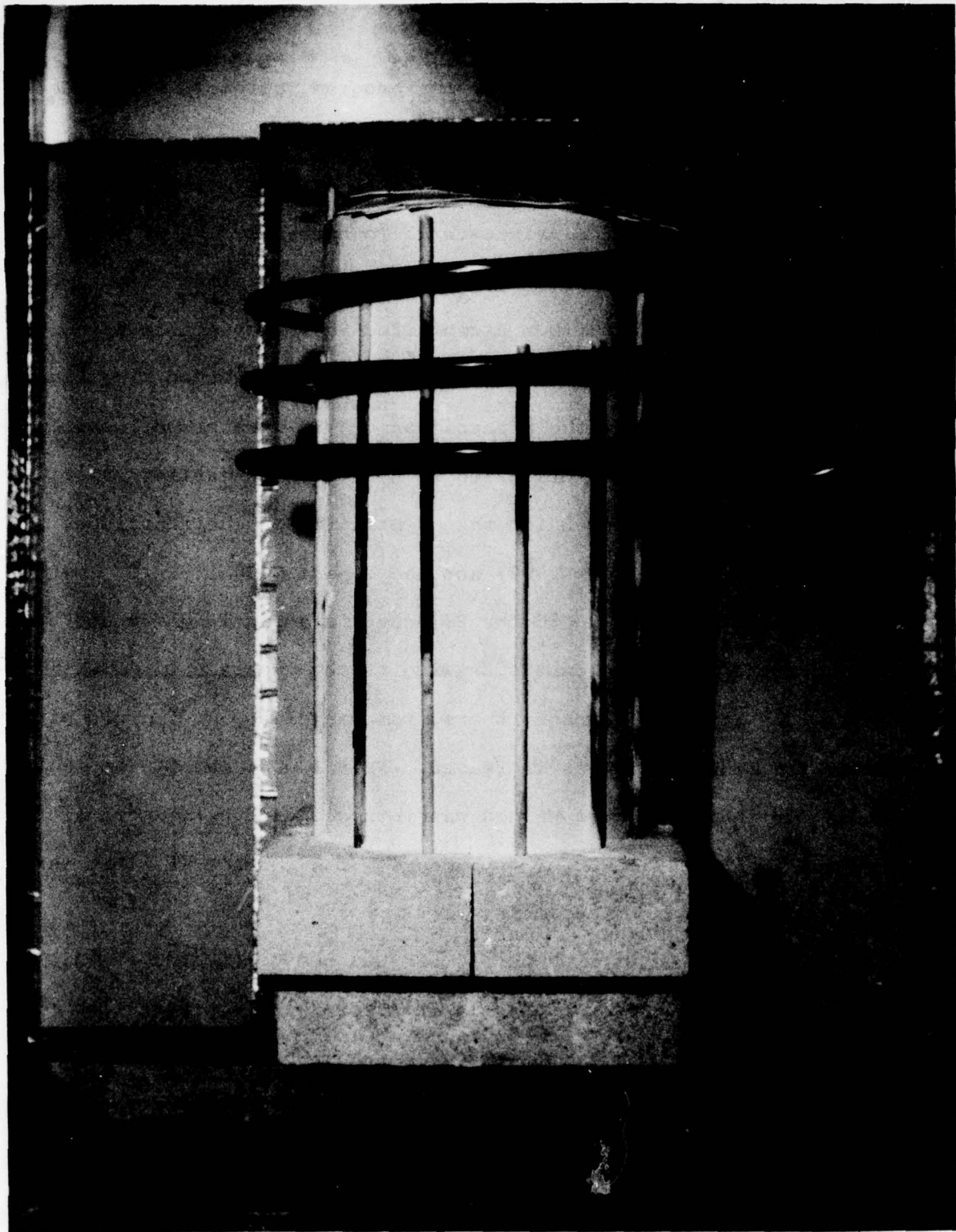


Figure 2. Apparatus for Skull Melting.

During the last few months of our program, attempts were made to grow crystals of YF_3 . Sources of high purity YF_3 were difficult to find since a hydrofluorination reaction is required at elevated temperatures. One must be particularly careful to have only YF_3 or else the phase equilibria, transitions, and purity greatly complicate the single crystal growth. This is further exemplified in YF_3 by a transition from a hexagonal to orthorhombic form which may be governed kinetically. An excellent procedure for the preparation of YF_3 free of OH^- , oxyfluoride, and residual oxide was discussed in detail in an earlier report⁽⁴⁾ and this process was followed for the preparation of the fluorides. Briefly, high purity Y_2O_3 (99.999) and the dopant CeO_2 or Pr_6O_{11} were hydrofluorinated at 1000-1200°C for 24 hours in a platinum furnace chamber. Figure 3 is a schematic drawing of the apparatus. After loading the oxides into the furnace, the system was closed and purged with N_2 gas as the temperature was increased. Near 1000°C the N_2 was shut off and a continuous flow of HF gas was introduced. The temperature was then raised to about 1200°C for five hours. The furnace was then turned off and cooled to room temperature.

The preparation of high purity LiF was not considered in this program since it is readily available in a pure single crystalline form of 99.99% analysis from sources such as Harshaw Chemical Company. In this form it can be broken and mixed with the YF_3 just prior to growth, thus minimizing storage and contamination problems. The same procedure was followed with the use of KF to prepare KY_3F_{10} . Caution must be followed in the amount of HF or compounds such as KHF_2 may form as a precipitate.

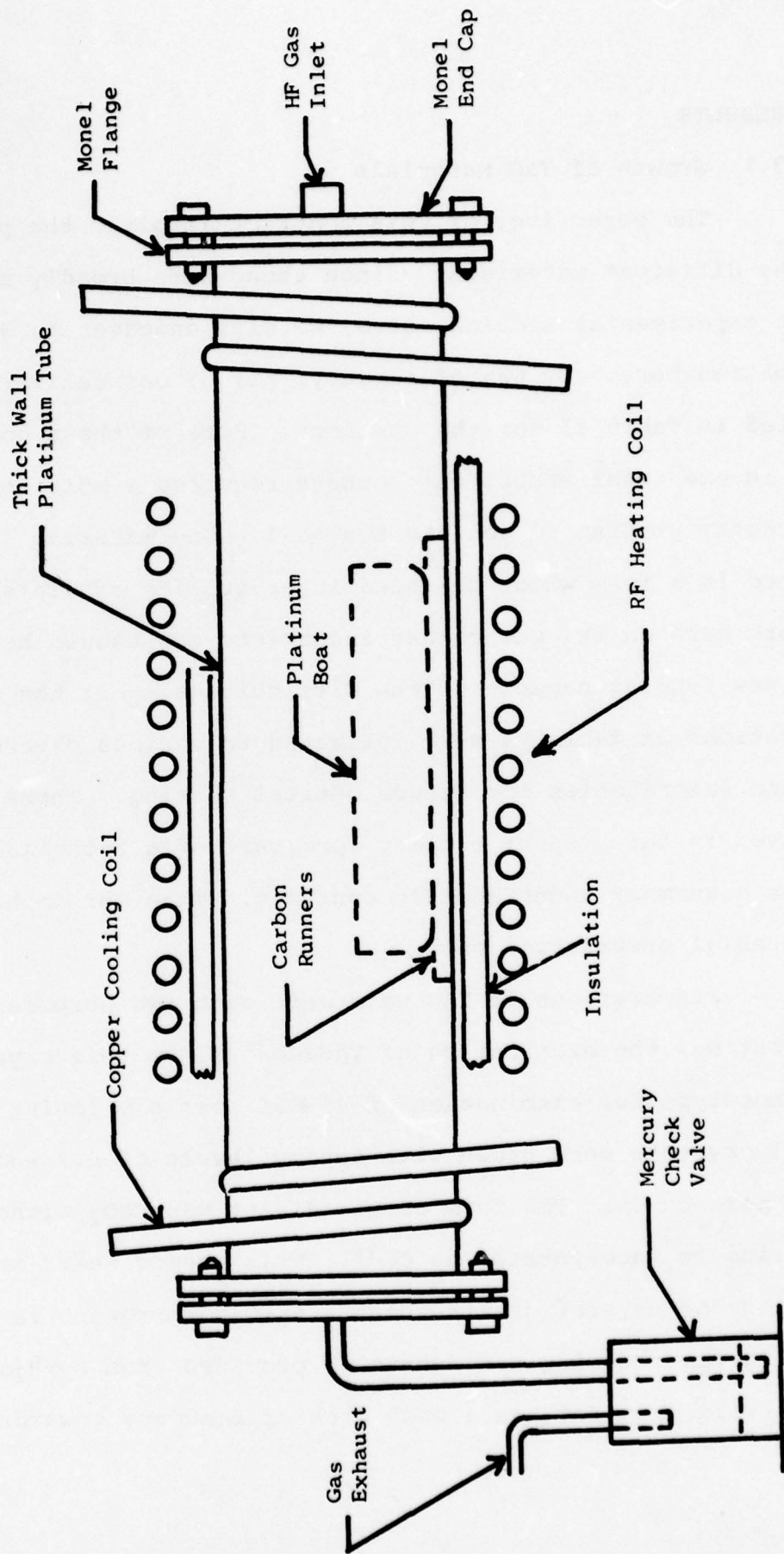


Figure 3. Drawing and construction of hydrofluorination apparatus.

3.0 RESULTS

3.1 Growth of YAG Materials

The objectives of this contract involved the preparation of many different materials. Since these were broadly classified in the experimental section above, we will endeavor to detail more information here. By way of summary, all of our deliveries are compiled in Table II for the contract. Some of these could be prepared in one trial experiment; others required a more comprehensive and lengthy program to achieve the goal. One material (YF_3) was prepared in a form which demanded laser quality crystals of cm size. The work here on YF_3 was rather incomplete and should be continued under new funding because of the difficulties. All the crystal preparations of Table II were delivered to various government or academic laboratories for future optical testing. These tests are not given in this report but may form part of a technical publication or a summary under another contract. Thus our emphasis is on the material preparation only.

Preparations of YAG were made with two purposes in mind. The first was the examination of $YAG:Ce^{3+}$ since this crystal served as a prototype for examination of $4f \rightarrow 5d$ possible lasing systems. Several crystals were grown with doping levels of 0.1 and 0.5 atomic percent Ce. The form of the dopant was CeO_2 although most of the cerium is incorporated as Ce^{3+} . This occurs under oxidizing conditions of crystal growth where a N_2-O_2 atmosphere is utilized. If a slightly reducing atmosphere is provided from N_2-H_2 , the crystal will grow but has a much greater tendency towards cracking.

TABLE II

SUMMARY OF DELIVERED ITEMS

<u>Shipment</u>	<u>Number of Items</u>	<u>Item Description</u>
1	2	YAG:Ce
2	1	ZrO ₂ :Ce
3	7	YAG:Er, Yb
4	2	ZrO ₂ :Ce - Ca
5	2	ZrO ₂ :Ce - Y
6	1	KY ₃ F ₁₀ :Pr
7	1	ZrO ₂ :Ce
8	2	ZrO ₂ , KY ₃ F ₁₀ :Ce
9	3	YAG:Ce
10	7	YF ₃ :Ce, CeO ₂
11	8	ThO ₂
12	6	ThO ₂ :Ce
13	1	YF ₃ :Pr
14	1	YAG:Ce
15	2	YAG:Er, Yb

The amount of Ce^{3+} is also increased but complete conversion is probably never attained. The reason for this may lie in the much larger radius of Ce^{3+} compared to Ce^{4+} . In the garnet structure large rare earths tend to substitute on the dodecahedral sites exclusively. Another difficulty of growth is connected with the low distribution coefficient of Ce. This has been estimated⁽⁵⁾ to be about 0.1 for Ce^{3+} in YAG. No experiment measurements have been made thus far in our laboratory. Our materials were prepared in several forms such as cylindrical rods, disks, or parallelepipeds of various dimensions. The latter were polished selectively to laser specifications on one, two, or three pairs of opposing faces. AR coatings were applied for particular wavelengths. These were usually in the range of 480-530 nm.

The other YAG material which we provided was a series of seven rectangular parallelepiped each 3 x 3 x 6 mm and polished on all six faces. The crystals were doped with 1, 5, 10, and 20% Er for one series. Another series was doped simultaneously with Er and Yb. The Er was fixed at 1% while the Yb was changed to 5, 10, and 20%. These samples should provide a basic understanding of any spectral effects due to concentration differences. The purpose and value of the YAG:Er,Yb system lies in the fact that laser action around $3\mu m$ can be obtained. Some preliminary reports have been given^(6,7) and results are promising. Our work should be continued to the actual examination of laser rods prepared from high quality boules of YAG:Er,Yb. Since both Er and Yb have atomic radii very close to that of Y, there is apparently no limit on the

amount of substitution. Boule quality remains good at all levels of Er and Yb with which we have experimented.

3.2 Growth of Fluorite Structured Oxides

The broad objective of this part of our effort was to incorporate Ce^{3+} into single crystal fluorite structured oxides. Various complications may occur in these systems such as stabilization to the cubic form, color center formation due to defect formation from oxygen vacancies, valence control of Ce to obtain high levels of Ce^{3+} , possible charge compensation schemes, and simple high temperature preparation methods. Our procedures were directed towards two types of preparations, i.e. the polycrystalline sintered oxides and finally single crystals.

3.2.1 Polycrystalline Preparations

Sintered polycrystals have an enormous advantage over a single crystal if only a limited amount of data are sought. The advantages are that large numbers of preparations can be made, costs are very small, and times are short. Thus several optical parameters such as fluorescence spectra, lifetimes, and absorption can be obtained readily. If satisfactory measurements are found, these can be followed later by more refined single crystals.

All of our sintered preparations of ZrO_2 were processed by mixing the respective oxides, pressing a small cylinder isostatically, or hydraulically, and then heating in an iridium crucible for 12-24 hours at a temperature of 2000-2200°C. Atmosphere control was maintained by mixing either 1-2% H_2 or O_2 with N_2 as an inert carrier. The sintered preparation was powdered by

mechanical work after the outer surface layer was removed. This layer consisted of a small amount of transported Ir or IrO₂ which blackened the sample slightly. Sample interiors showed no evidence of iridium.

The first samples were prepared to examine the nature of various stabilizers in ZrO₂ and their effects on the dopant of CeO₂. To this end CaO, Y₂O₃ and MgO were added in the range of 5-15 mole% to ZrO₂ while CeO₂ was held constant at 0.1%. Next the problem of charge compensation of Ce³⁺ was examined. This was approached by the addition of either Na⁺ or Ta⁵⁺ in a series of samples where the Y₂O₃ stabilizer and dopant were held constant. Excitation and fluorescence spectra were obtained for these samples. The amount of Ce³⁺ which can be incorporated into ZrO₂ is partially a function of the chemical atmosphere. Furthermore the crystal structure of CeO₂ is that of ZrO₂ at high temperatures and in O₂ atmosphere. Some data were collected on CeO₂ which was sintered in either O₂ or H₂. Various amounts of Ta⁵⁺ were then added (0.1, 1.0, and 5%) for charge compensation of Ce³⁺. All samples were again sintered in H₂ or O₂. The excitation and fluorescence spectra were recorded.

One of the manifest disadvantages of ZrO₂ or HfO₂ is that the cubic structure has to be stabilized by the addition of aliovalent ions in the form of high melting oxides. Thus one immediately is faced with possible absorption centers associated with the defect chemistry. In order to circumvent this situation, one may work with ThO₂ which possesses a cubic structure without

concurrent stabilizers. ThO_2 has an extremely high melting point of 3300°C , is an α -emitter, and very little work has been done on single crystal growth. Possible methods are flux growth or skull melting. Prior to undertaking more extensive work on growing single crystals, some preliminary preparations were again examined by sintering and diffusion in Ir crucibles. The main interest lies in the Ce^{3+} doped ThO_2 as the additive. The control of the Ce valence was again attempted by choice of oxidizing (O_2) or reducing (H_2) gases. Samples were prepared in pairs according to the gas. The first pair was composed of only ThO_2 with no dopant. The second pair was composed of ThO_2 and 0.5 mole % CeO_2 . The third pair combined ThO_2 , 0.5 mole % CeO_2 , and 0.5 mole % Ta_2O_5 for possible charge compensation. The final pair combined ThO_2 , 0.5 mole % CeO_2 and 5.0 mole % Ta_2O_5 . Samples were heated to 1900°C in the form of pressed powders. The samples were cleaned of any surface iridium and then examined spectroscopically for absorption and fluorescence. In addition to trying Ta^{5+} as a charge compensator for Ce^{3+} , the use of Na^+ was also suggested. Na^+ is probably more volatile at sintering temperatures close to 2000°C but an effort was made for additions to ThO_2 . Pairs of samples were chosen with O_2 or H_2 atmospheres. Samples were chosen from pure ThO_2 , 0.5% CeO_2 plus 0.25% Na as Na_2CO_3 , and 0.5% CeO_2 plus 2.5 mole % Na_2CO_3 . The pellet method was utilized for sintering. Results were judged by spectroscopic methods.

3.2.2 Single Crystals

Only a few preparations of single crystals were completed during this contract. A modified skull melting process was developed for stabilized ZrO_2 . The usual dopant was CeO_2 . At the present time there was no provision for containment of the entire process in selected atmospheres of H_2 or O_2 . Likewise the use of ThO_2 was not attempted because all raw materials were finely divided powders. These are likely to be dispersed throughout the laboratory and equipment if not enclosed properly. Thus both the personnel and area should be protected and isolated from this alpha emitter.

Some of the first experiments were directed towards ZrO_2 stabilized with Y_2O_3 . An important factor is the actual band gap of this material. Preferably with the Ce doping, the band gap should lie above 50000 cm^{-1} (6.2 eV or $0.2\text{ }\mu\text{m}$). This energy is of the order of separation between 4 f and 5 d states in Ce^{3+} but is probably lower in oxidic hosts. Our first single crystals were prepared with about 7% Y_2O_3 . These crystals all gave fundamental absorption edges around $0.33\text{ }\mu\text{m}$. Probably this is due to the defect chemistry of these stabilized oxides. Higher proportions of Y_2O_3 did not change the situation. A possible alternative might be to grow the crystal in O_2 but this was not tried. The presence of excited state absorption in YAG:Ce suggests that a similar effect may occur in ZrO_2 :Ce. However the high absorption in the region $0.2 - 0.3\text{ }\mu\text{m}$ would probably obscure some of the peaks. Some of the crystals we have grown of undoped ZrO_2 are shown in Figure 4. The crystals were cut in 2-3 mm thicknesses, polished, and examined optically. Some of these slices were also exposed to flash lamps, ultraviolet lamps, x-rays, and

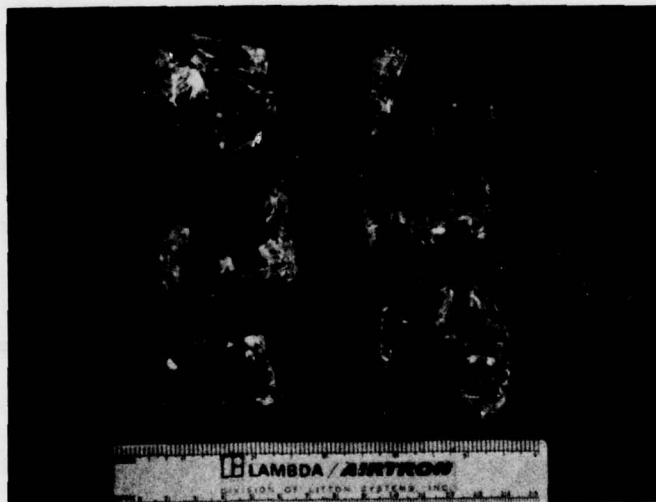


Figure 4. Single Crystals of ZrO_2 .

sunlight. Additional color centers were difficult to introduce and little darkening was observed. This area is worthy of more investigation with crystals prepared from two sources such as flux and skull growth. The former source is valuable for low temperature preparation and should not be highly oxygen deficient.

Several runs were made of single crystal ZrO_2 doped with CeO_2 . Among these were the use of various stabilizers such as MgO , Y_2O_3 , and CaO . The concentration of Ce was adjusted to 0.1 mole % in all cases. These runs yielded single crystals in cm sizes and were examined optically for fluorescence behavior at several laboratories. The incorporation of Ce^{3+} for Zr^{4+} presents a problem of charge compensation, atmosphere control, and oxide volatility. A few experiments were made to alleviate the problem by the addition of either Ta_2O_5 or Na_2O . In the first case charge is balanced via $2 Zr^{4+} \rightarrow Ta^{5+} + Ce^{3+}$ and in the second case via $Zr^{4+} \rightarrow Ce^{3+} + Na^+$. The principle difficulty lies in the vapor pressure of these oxides at the ZrO_2 melting point. To correct for volatility, a 50/1 excess, i.e. 5 mole % Ta or Na was added along with 0.1 mole % CeO_2 . Crystals were grown and spectra were recorded as before. One of the big unknowns is the amount of Ta^{5+} or Na^+ incorporated into the crystal compared to that in the melt at the same temperature. This simply is a distribution coefficient and ordinarily the melt composition is equivalent to that prepared at room temperature. In our situation almost all oxides are volatile; the loss of these elements prevents stable equilibria. Analytical data will be dependent on conditions of each experiment. Thus far we have not measured any effective distributions but such data are needed.

3.3 Growth of Fluorides

Single crystals of YF_3 were grown in a special apparatus where an HF atmosphere could be maintained. This atmosphere was 98% N_2 and 2% HF by volume. A schematic diagram of the growth apparatus is shown in Figure 5.

The phase equilibrium diagram for the LiF- YF_3 system (Figure 6) indicates that the compound YF_3 melts congruently at $1150^\circ C$. A polymorphic phase transition from hexagonal to an orthorhombic structure occurs in YF_3 at about $1050^\circ C$. The first series of single crystal growth runs started with the stoichiometric composition. Severe cracking of the pulled boules indicated that the polymorphic transition was destructive and large crystals would be difficult if not impossible to grow. In order to avoid the transition, YF_3 was grown from solution in the YF_3 -LiF system. As long as the temperature of growth was between $1050^\circ C$ and $820^\circ C$ and the composition between about 50 and 80 mole % YF_3 , the destructive transition could be avoided. Several growth runs were completed under these conditions. Table III summarizes the results of the growth runs of Ce or Pr doped YF_3 . X-ray diffraction of the pulled crystal identified YF_3 . The melt was then compensated with polycrystalline YF_3 to obtain the desired starting composition for the next run.

Since seed crystals of YF_3 were not available at the start of the experiments, a platinum wire was used for nucleation. Eventually sufficient size single crystal pieces of YF_3 were obtained and could be used for seeds. Figures 7 and 8 show several crystals.

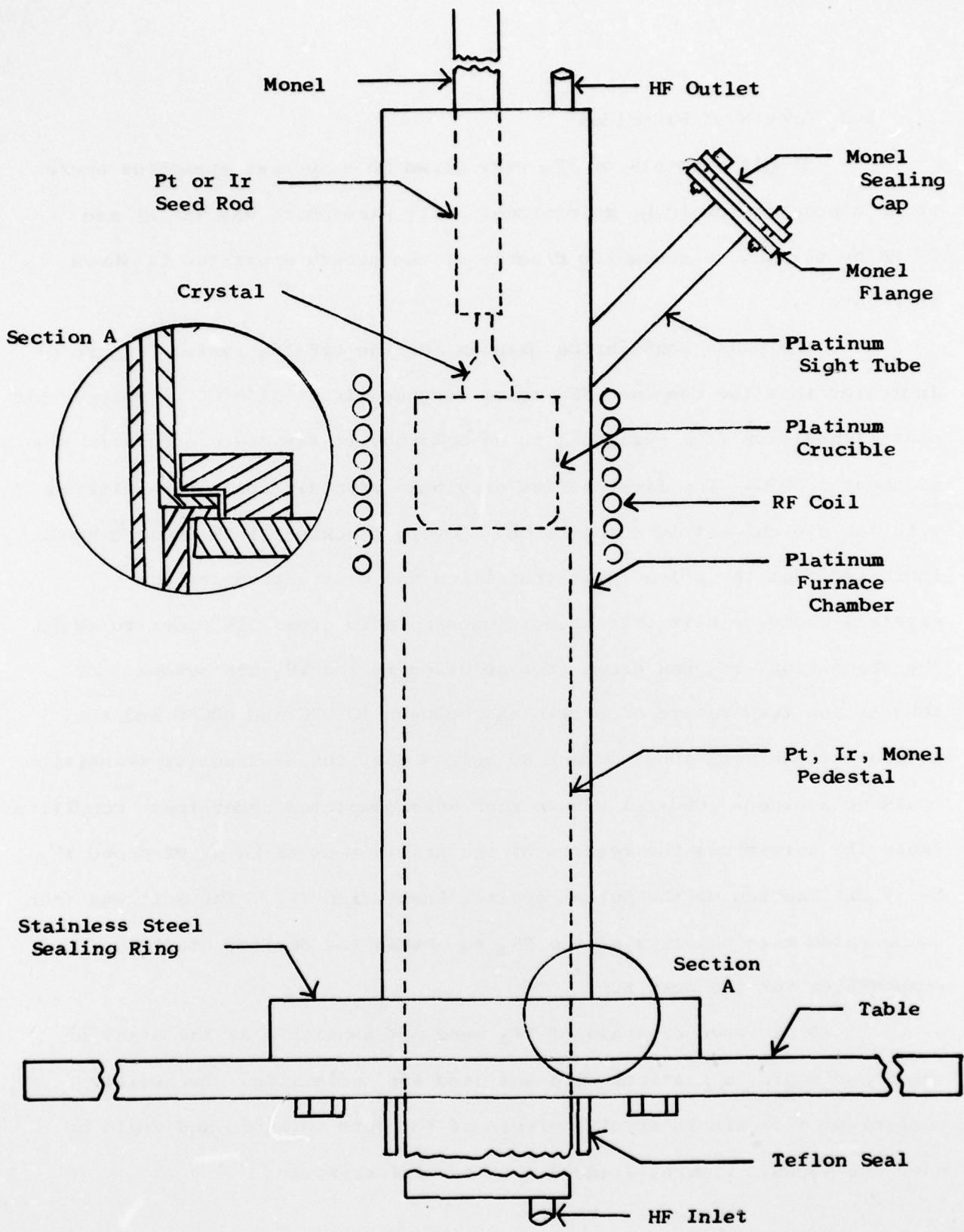


Figure 5. Drawing of crystal growth apparatus.

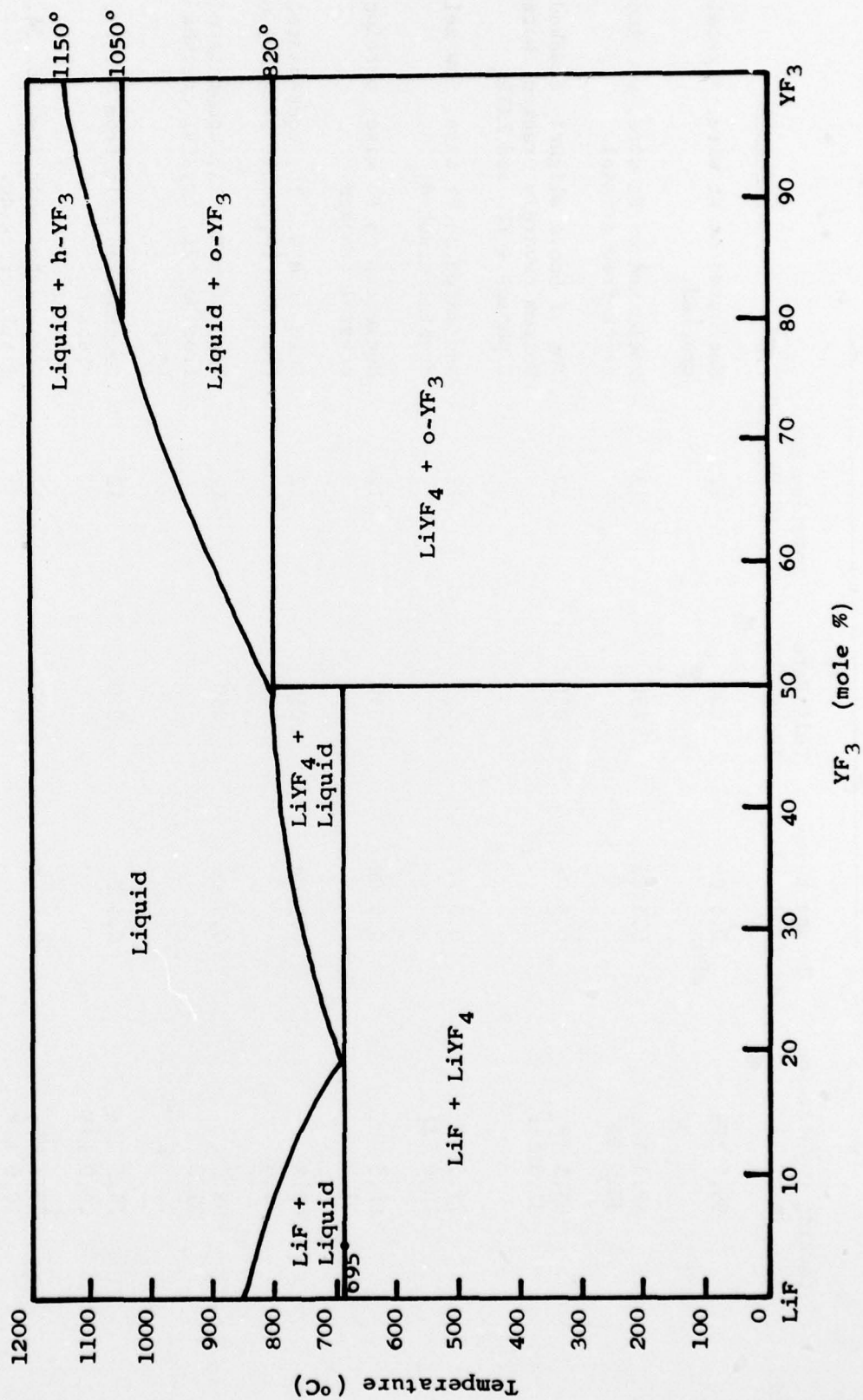


Figure 6. Phase diagram of LiF-YF₃ system.

Table III

SINGLE CRYSTAL GROWTH RUNS OF Ce OR Pr DOPED YF₃

<u>Run No.</u>	<u>Starting Composition (mole %)</u>	<u>Dopant Level (mole %)</u>	<u>Pull Rate inches/hr</u>	<u>Rotation Rate (RPM)</u>	<u>Comments</u>
25	99.5 YF ₃	0.5 Ce	.050	12	Nucleated on Pt wire, crystal severely cracked.
25A	69.5 YF ₃ 30.0 LiF	0.5 Ce	.050	12	Nucleated on Pt wire, sections of crack-free crystal.
28	68.5 YF ₃ 31.0 LiF	0.5 Ce	.050	12	Top of boule slightly cracked, bottom severely cracked; bottom showed 2 phases - YF ₃ and LiYF ₄
29	79.5 YF ₃ 20.0 LiF	0.5 Pr	.050	12	Nucleated on Pt wire, new melt, crystal cracked.
30	68.5 31.0	0.5 Ce	.050	12	Nucleated on Pt wire, portion of crystal cracked.
31	68.5 31.0	0.5 Ce	.050	12	Seed from No. 30, compensated melt from No. 29, boule slightly cracked.
33	68.5 31.0	0.5 Ce	.050	12	Seed from No. 31, compensated melt from No. 31, crystal cracked and hazy.
34	74.5 YF ₃ 25.0 LiF	0.5 Pr	.050	12	Compensated melt from No. 29, slight cracking.
35	79.5 YF ₃ 20.0 LiF	0.5 Pr	.050	12	Compensated melt from No. 34, very little cracking.
36	67.0 YF ₃ 32.5 LiF	0.5 Pr	.050	12	Compensated melt from No. 35, crystal severely cracked.
38	68.5 YF ₃ 31.0 LiF	0.5 Pr	.050	12	New melt, crystal hazy.

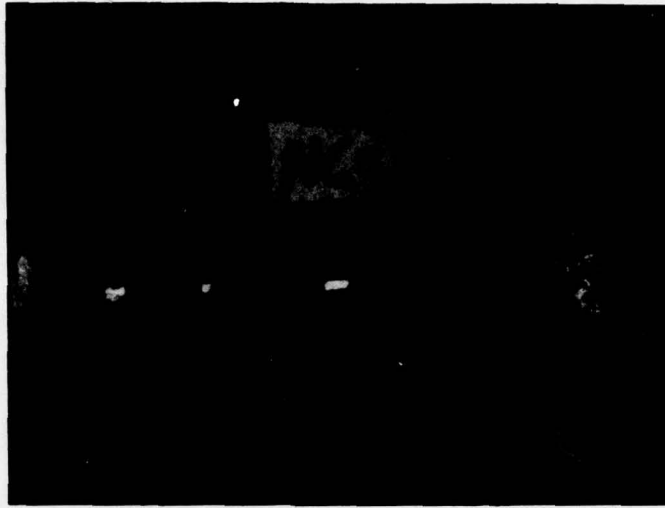


Figure 7. Pr:YF₃ crystal.



Figure 8. Pr:YF₃ crystal.

A few single crystals of $KY_3F_{10} : Pr$ were prepared by mixing KF , YF_3 , and PrF_3 . The phase diagram of the $KF-YF_3$ system is quite complicated but the compound KY_3F_{10} can be crystallized as a congruently melting cubic crystal with a melting point around $1000^\circ C$. Our preparation utilized single crystal KF from Harshaw Chemical Company and a hydrofluorinated mixture of Y_2O_3 and Pr_6O_{11} . The latter were 99.99% oxides from Research Chemical or other sources. The fluorides were mixed in a platinum container, brought to the melting point under an atmosphere of argon and HF , and allowed to crystallize freely in the crucible. Large single crystals of cm size were obtained and identified by X-ray diffraction. The crystals were cut in the form of 5mm cubes, polished on all faces, and submitted for spectroscopic evaluation. A few attempts were made on growth by seeding via a Czochralski technique. Seeds were obtained from large crystal pieces extracted from a melt. These were cut, oriented, and mounted. In general the crystal quality was good but in some cases cloudy material was obtained. This was found to be related to growth conditions or formation of precipitates of other phases in the $KF-YF_3$ system. The presence of KHF_2 cannot be excluded but this could be eliminated by using argon with no HF .

4.0 CONCLUSIONS

The introduction of Ce^{3+} and other rare earths into fluorite structured materials appears to be difficult under most circumstances. Mixed fluorides offer some hope but most systems are composed of unknown phase diagrams. Single crystals of a few different compounds were prepared with limited success in $LiF-YF_3$ or $KF-YF_3$ systems. In oxide systems all compounds are high melting, require stabilizing ions for cubic phases, or present problems of radioactivity. Further work on ThO_2 may be beneficial since stabilizers are not required. Special skull melting procedures have to be developed for handling and growing ThO_2 single crystals. Fluorite structured hosts always will require some form of charge compensation since R^{3+} are substituting for R^{2+} or R^{4+} . With skull melting preparations, the oxide volatility introduces complications but can probably be done by element selection and atmosphere control.

REFERENCES

1. G. Blasse and A. Brill, Appl. Phys. Letters 11, 53 (1967).
2. G. Blasse and A. Brill., J. Chem. Phys. 47, 5139 (1967).
3. R.R. Jacobs, W.F. Krupke, and M.J. Weber, Appl. Phys. Letters 33, 410 (1978).
4. W.J. Miniscalco, J.M. Pellegrino, and W.M. Yen, J. Appl. Phys. 49, 6109 (1978).
5. R.R. Monchamp, J. Crystal Growth 11, 310 (1971).
6. E.V. Zharikov, et al., Sov. J. Quant. Electron. 4, 1039 (1975).
7. A.M. Prokharov et al., Phys. Stat. Sol. (a) 40, K69 (1977).